Wyoming Water Research Program
Annual Technical Report
FY 2014

Introduction

The NIWR/State of Wyoming Water Research Program (WRP) coordinates participation in the NIWR program through the University of Wyoming's Office of Water Programs (OWP). The primary purposes of the WRP are to support and coordinate research relative to important water resources problems of the State and Region, support the training of scientists in relevant water resource fields, and promote the dissemination and application of the results of water-related research.

Primary participants in the WRP are the USGS, the WWDC, and the University of Wyoming. An advisory committee, consisting of representatives from State and Federal agencies, solicits and identifies research needs, recommends projects, and reviews and monitors project progress. The Director of the OWP serves as a point of coordination for all activities and serves to encourage research by the University of Wyoming addressing the needs identified by the advisory committee. State support for the WRP includes direct funding through the WWDC and active State participation in identifying research needs and project selection and oversight.

The WRP supports faculty and students in University of Wyoming academic departments. Faculty acquire their funding through competitive peer reviewed grants. Since its inception in the year 2000, the WRP has funded a wide array of water related projects across several academic departments.

Research Program Introduction

Since inception of the NIWR program in 1965, the Wyoming designated program participant has been the University of Wyoming. Until 1998, the Wyoming NIWR program was housed in the Wyoming Water Resources Center (WWRC). However, in 1998 the WWRC was closed. In late 1999, the Wyoming Water Research Program (WRP) was initiated to oversee the coordination of the Wyoming participation in the NIWR program. The primary purpose of the Wyoming Institute beginning with FY00 has been to identify and support water-related research and education. The WRP supports research and education by existing academic departments rather than performing research in-house. Faculty acquire funding through competitive peer-reviewed proposals.

In conjunction with the WRP, an Office of Water Programs (OWP) was established by State Legislative action beginning July 2002. The duties of the Office are specified by the legislation as: (1) to work directly with the Director of the Wyoming Water Development Office to identify research needs of State and Federal agencies regarding Wyoming water resources, including funding under the National Institutes of Water Resources (NIWR), (2) to serve as a point of coordination for and to encourage research activities by the University of Wyoming to address research needs, and (3) to submit a report annually prior to each legislative session to the Select Water Committee and the Wyoming Water Development Commission on the activities of the office.

The WRP, which is coordinated through the OWP, is a cooperative Federal, State, and University effort. Activities are supported by the NIWR, Wyoming Water Development Commission, and University of Wyoming. A State Advisory Committee serves to identify research priorities, recommend projects for funding, and monitor project progress. Reports for the following FY14 WRP research projects are given herein in the order listed below:

Project 2012WY81B Final Report: Multi-Frequency Radar and Precipitation Probe Analysis of the Impact of Glaciogenic Cloud Seeding on Snow, Bart Geerts, Prof., Dept. of Atmospheric Science, UW, Mar 2012 thru Feb 2015.

Project 2012WY82B Final Report: Decadal Scale Estimates of Forest Water Yield After Bark Beetle Epidemics in Southern Wyoming, Brent E. Ewers, Assoc. Prof., Dept. of Botany; Elise Pendall, Assoc. Prof., Dept. of Botany and Program in Ecology; Urszula Norton, Asst. Prof., Plant Sciences Dept.; and Ramesh Sivanpillai, Academic Professional Research Scientist, WyGISC/Dept. of Botany, UW, Mar 2012 thru Feb 2015.

Project 2013WY84B Final Report: Mapping Annual Surface Area Changes Since 1984 of Lakes and Reservoirs in Wyoming that are not Gauged Using Multi-Temporal Landsat Data, Ramesh Sivanpillai, Senior Research Scientist – Extended Term, Dept.of Botany & Wyoming Geographic Info Science Center (WyGISC), UW, Mar 2013 – Feb 2014 (Extended through Feb 2015).

Project 2013WY85B Final Report: Micro-Patterned Membrane Surfaces with Switchable Hydrophobicity, Carl P. Frick, Assist. Prof., Dept. of Mechanical Engr., and Jonathan A. Brant, Assist. Prof., Dept. of Civil and Architectural Engr., UW, Mar 2013 – Feb 2015.

Project 2013WY86B Annual Report: Use of Fe(VI) for the Improvement of Water Quality in Wyoming, Maohong Fan, SER Assoc. Prof., Dept. of Chemical & Petroleum Engr., and Lamia Goual Assist. Prof., Dept. of Chemical and Petroleum Engr., UW, Mar 2013 – Feb 2016.

Project 2013WY87B Annual Report: Rumen Microbial Changes Associated with High Sulfur -- A Basis for Developing Treatments for Ruminant Livestock in High Sulfur Water Regions, Kristi M. Cammack, Assist. Prof. and Kathy J. Austin, Research Scientist, Animal Science, UW; Cody L. Wright, Ph.D., Prof. and Ken Olson, Assoc. Prof., Animal Science, S. D. State Univ.; and Gavin Conant, Assist. Prof. and William Lamberson, Prof., Animal Sciences, Univ. of Missouri, Mar 2013 – Feb 2016.

Multi-frequency Radar and Precipitation Probe Analysis of the Impact of Glaciogenic Cloud Seeding on Snow

Basic Information

Title:	Multi-frequency Radar and Precipitation Probe Analysis of the Impact of Glaciogenic Cloud Seeding on Snow
Project Number:	2012WY81B
Start Date:	3/1/2013
End Date:	2/29/2016
Funding Source:	104B
Congressional District:	1
Research Category:	Climate and Hydrologic Processes
Focus Category:	Water Quantity, Climatological Processes, Hydrology
Descriptors:	None
Principal Investigators:	Bart Geerts

Publications

1. Yang, Yang, 2013. Snow transport patterns in orographic storms as estimated from airborne vertical-plane dual-Doppler radar data, MS Thesis, Atmospheric Science, UW, Dec, 47 pgs.
2. Chu, Xia, 2013. Cloud-resolving Large Eddy Simulations of the silver idodide dispersion from ground and its impact on orographic clouds and precipitation, MS Thesis, Atmospheric Science, UW, August, 97 pgs.
3. Miao, Q., and B. Geerts, 2013: Airborne measurements of the impact of ground-based glaciogenic cloud seeding on orographic precipitation. Advances in Atmospheric Science, 30, 1025-1038. doi: 10.1007/s00376-012-2128-2.
4. Geerts, B. and co-authors, 2013: The AgI Seeding Cloud Impact Investigation (ASCII) campaign 2012: overview and preliminary results. J. Wea. Mod., 45, 24-43.
5. Xue, L., X. Chu, R. Rasmussen, D. Breed, B. Boe, B. Geerts, 2014: The dispersion of silver iodide particles from ground-based. Part II: WRF Large-Eddy Simulations v.s. observations. J. Appl. Meteor. Climatol., 53, 940-958.
6. Pokharel, B., B. Geerts, and X. Jing, 2014a: The impact of ground-based glaciogenic seeding on orographic clouds and precipitation: a multi-sensor case study. J. Appl. Meteor. Climat., 53, 890-909. (21 Feb 2012 case study).
7. Boe, B., and co-authors, 2014: The dispersion of silver iodide particles from ground-based generators over complex terrain. Part I: Observations with acoustic ice nucleus counters. J. Appl. Meteor. Climatol.,53, 1325–1341.
8. Pokharel, B., B. Geerts, X. Jing, K. Friedrich, J. Aikins, D. Breed, R. Rasmussen, and A. Huggins, 2014b: The impact of ground-based glaciogenic seeding on clouds and precipitation over mountains: a multi-sensor case study of shallow precipitating orographic cumuli. Atmos. Res., 147, 162-182. (13 Feb 2012 case study) http://dx.doi.org/10.1016/j.atmosres.2014.05.014
9. Pokharel, B., and B. Geerts, 2014: The impact of glaciogenic seeding on snowfall from shallow orographic clouds over the Medicine Bow Mountains in Wyoming. J. Wea. Mod. , 46, 8-29.
10. Chu, X., B. Geerts, L. Xue, and R. Rasmussen, 2014: Radar observations and WRF LES simulations of the impact of ground-based glaciogenic seeding effect on orographic clouds and precipitation: Part

I: Observations and model validations. J. Appl. Meteor. Climat., 53, 2264-2286.

11. Geerts, B., Y. Yang, R. Rasmussen, S. Haimov, and B. Pokharel, 2015: Snow growth and transport patterns in orographic storms as estimated from airborne vertical-plane dual-Doppler radar data. Mon. Wea. Rev. , 143, 644-665.
12. Jing, Xiaogin, 2014. Dual-polarization radar data analysis of the impact of ground-based glaciogenic seeding on winter orographic clouds, MS Thesis, Atmospheric Science, UW, August, 82 pgs.
13. Poklarel, Binod, 2014. A multi-sensor study of the impact of ground-based glaciogenic seeding on orographic clouds and precipitation, Ph.D. Dissertation, UW, Dept. of Atmospheric Science, December, 204 pgs.

Multi-frequency radar and precipitation probe analysis of the impact of glaciogenic cloud seeding on snow

Final Report
(Mar 2012 – Feb 2015)
UW Office of Water Programs
U. S. Geological Survey and the Wyoming Water Development Commission grant
Dr. Bart Geerts, PI
5/1/2015

1. Abstract

This proposal (referred to as Cloud Seeding III) called for the analysis of radar, aircraft, and ground-based datasets collected as part of the ASCII (AgI Seeding Cloud Impact Investigation) campaign over the Medicine Bow mountains and the Sierra Madre in Wyoming during the time of glaciogenic cloud seeding conducted as part of the multi-year Wyoming Weather Modification Pilot Project (WWMPP). The WWMPP is a randomized mountain-blind seeding experiment using a series of silver iodide (AgI) generators located in both mountain ranges.

Two previous UW Office of Water Programs grants (referred to as Cloud Seeding I and Cloud Seeding II) supported seven research flights over the Snowy Range. Analysis of these data led to a remarkable paper in the *J. Atmos. Sci.* (Geerts et al. 2010), which was important in the success of a proposal for the ASCII (AgI Seeding Cloud Impact Investigation) campaign, funded by the National Science Foundation [AGS-1058426: "The cloud microphysical effects of ground-based glaciogenic seeding of orographic clouds: new observational and modeling tools to study an old problem." Aug 2011 – Jul 2015]. The ASCII campaign was the first glaciogenic cloud seeding project sponsored by NSF in about 25 years. The two previous UW Office of Water Programs "seed" grants, the Geerts et al. (2010) paper, the NSF grant, and the ASCII campaign itself were all important in the 2012 National Institutes of Water Resources (NIWR) "IMPACT" Award to the PI (Dr. Geerts), a national recognition initiated by the UW Office of Water Programs.

The third UW Office of Water Programs grant (referred to as Cloud Seeding III) ran in parallel with ASCII. It complemented the NSF funds, especially allowing more graduate student participation. The mutual leveraging between federal and Office of Water Programs funds resulted in an accomplishment larger than the sum of the two grants. *The combined grants (which are truly inseparable) have enabled three MSc degrees and 2 PhD degrees, have led to the publication of no less than 18 peer-reviewed papers, and have supported numerous presentations at conferences and WWMPP meetings.*

2. Objectives and methodology

The key objective is to examine the impact of glaciogenic seeding of orographic clouds on cloud and precipitation. The methodology is described in Geerts et al. (2013) and Pokharel and Geerts (2014).

3. Summary of the field work and principal findings

Most of the 25 storms sampled in ASCII occurred in unblocked flow, were non-frontal and rather shallow, produced light natural snowfall (0.4-0.6 mm hr-1 on average), had rather cold cloud bases (-9°C on average), and had rather little SLW (<0.4 mm vertically integrated liquid in all cases). Several case studies emerged from ASCII. A study of a stratiform orographic cloud with few natural ice crystals (Pokharel et al. 2014a) revealed an increase in ice crystal concentration, according to disdrometer data in the target area, and an increase in low-level reflectivity, according to data from the ground-based and airborne radar systems, each with their own target and control regions. Of all studies ASCII cases, this case had the largest reflectivity increase in the target region, relative to the trend in the control region. This increase was ~4 dBZ for the DOW at low levels, corresponding to a near doubling of the precipitation rate.

Pokharel et al. (2014b) examined a case with small, shallow convective cells embedded in a larger weakly-precipitating, shallow stratiform snowfall emerging above a thin orographic stratiform cloud. Smaller but consistent increases in ice particle concentrations and near-surface reflectivity were observed, the latter mainly in the lee of the mountain in the target region. A consistent change in particle size distribution was observed at flight level, within the convective cells. . Pokharel et al. (2015a) examined the impact of seeding on an unusually "clean" shallow orographic cloud, confined between -5°C and 12°C, with large droplets (~35 μm) and few natural ice particles, most of them rimed. Small increases in reflectivity (1 dB) and ice particle concentrations (mainly of small particles) were observed in areas under cloud seeding compared to areas with no cloud seeding., without apparent change in the r Riming remained, which was the primary hydrometeor growth process during seeding. WCR reflectivity profiles suggest a strong seeding impact (at least in a relative sense), notwithstanding the very small liquid water path (<0.1 mm). This impact was confirmed by an LES model simulation with the Xue et al. (2013a,b) seeding parameterization (see next section).

Several ASCII-based composite studies have been conducted. Jing et al. (2015a) examined changes for six stratiform cases over the Sierra Madre, in terms of DOW polarization variables. They found evidence for increases in the concentration of unrimed dendritic ice crystals during seeding, and reflectivity which is consistent with the observed increase in differential reflectivity. Low-level reflectivity was higher on average and in all six individual cases, mainly at close range of the AgI generators, upwind of the mountain crest, which is about 18 km from the generators. Jing et al. (2015b) found that in three convective cases over the Sierra Madre, the seeding impact was more pronounced further downwind of the generators, i.e. in the lee, consistent with the convective case in Pokharel et al. (2014b).

Finally, a survey of all ASCII cases (Pokharel et al. 2015) shows that WCR, DOW, and snow gauge data all agree that, in most individual cases and on average, the precipitation rate was higher during seeding, at least in terms of a double difference (i.e., changes in the target region are compared to those in the control region) (**Fig. 1**). The average increase for all good cases (9-18 cases, depending on the instrument) ranges between 0.17-0.31 mm hr^{-1}, which is a significant fraction of the average natural precipitation rate. Pokharel et al. (2015) also examined the relationship between ambient and cloud conditions (such as cloud base and cloud top temperature, LWP, wind speed, and static stability) and affected seeding efficacy in ASCII reveals, but found no clear trends. This probably is due to a lack of cases and the noisiness of precipitation rate.

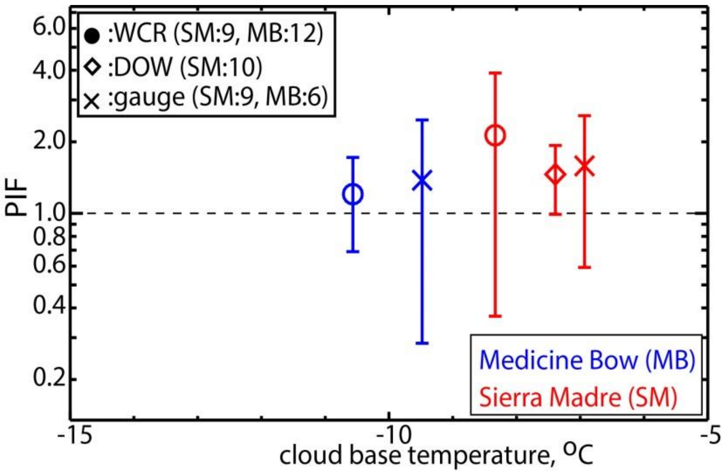

Fig. 1: Average change, ± one standard deviation, of precipitation rate during seeding, compared to an adjacent unseeded period, for all ASCII cases, based on three instruments. The precipitation impact factor (PIF) is a double ratio, defined as the seeded:unseeded ratio in the target area, compared to that in the control area. Here the PIF is plotted as a function of cloud base temperature. The number of cases for each instrument and each mountain range is shown between brackets.

All the ASCII case and composite studies highlight the challenge of signal detection within the highly variable, finely textured fields of cloud and precipitation particles. Not any single change reported in these studies can be attributed unambiguously to glaciogenic seeding. Signal detection remains the most significant challenge in observational weather modification research (see National Research Council 2003, Garstang et al. 2005).

4. Significance

Intellectual merit: A series of ASCII case studies (Pokharel et al. 2014a, b; Pokharel et al. 2015a, b; Chu et al. 2014) and composite observational studies (Geerts et al. 2013; Pokharel and Geerts 2014; Jing et al. 2015a; Jing and Geerts 2015; Pokharel et al. 2015b), mainly using the WCR and a DOW radar, consistently show an increase in radar reflectivity and (in most cases) in ice particle concentration at low levels downwind of AgI generators. Quantitative precipitation enhancement appears highly variable, remains difficult to measure, and is virtually impossible to predict based on environmental and cloud parameters alone. A separately funded collaborative effort, led by NCAR (Rasmussen, Xue et al.), reveals dramatic advances in the numerical modeling of artificial ice nucleation and cloud processes in mountain-scale large eddy simulations, which were tested in ASCII (Boe et al. 2014; Xue et al. 2014; Chu et al. 2014; Chu et al. 2015).

Broader Impact: Federal agencies including NSF extensively supported weather modification research in the 1960s-1980s. The ASCII campaign was the first glaciogenic cloud seeding project sponsored by NSF in about 25 years. The preponderance of evidence from an array of ASCII-supported publications (listed below) and separately funded collaborative modelling work supports the notion that glaciogenic seeding can significantly increase precipitation in shallow winter orographic clouds.

5. Peer-reviewed publications

The following 18 peer-reviewed papers were at least partly supported by this grant. As mentioned before, there is a significant overlap between this grant and the NSF ASCII grant, hence the statement "partly supported").

(1) An ASCII-12 overview paper can be found in Geerts et al. (2013).
(2) An ASCII-13 (plus pre-ASCII) overview paper can be found in Pokharel and Geerts (2014).
(3) Flight-level measurements of the impact of ground-based glaciogenic cloud seeding in plumes rising up to flight level are examined in Miao and Geerts (2013).
(4) Boe et al. (2014) and (5) Xue et al. (2014) examine the dispersion of AgI nuclei in the absence of clouds, using and acoustic ice nucleus counter and LES simulations respectively.
Binod Pokharel led three case study of the seeding impact on clouds and precipitation, i.e.,
(6) a shallow stratiform storm (21 Feb 2012 - Pokharel et al. 2014a),
(7) a shallow convective storm (13 Feb 2012- Pokharel et al. 2014b), and
(8) a stratiform cloud with large supercooled droplets (23 Feb 2012 – Pokharel et al. 2015a).
(9) a composite study of all ASCII cases, to examine how ambient and cloud conditions affect seeding efficacy in ASCII (Pokharel et al. 2015b).
A two-part paper in J. Appl. Meteor. Climat. explore numerical simulations of a stratified flow case under both seeded and natural conditions (18 Feb 2013):
(10) Chu et al. (2014) compare radar observations against WRF LES simulations; and
(11) Xue et al. (2015c) evaluate the microphysical changes due to seeding in model output.
(12) Geerts et al. (2015) examine snow growth, transport, and deposition patterns in both stratiform and convective orographic storms, using WCR profiling and dual-Doppler analyses for 15 storms over the Medicine Bow range.
(13) Jing et al. (2015) and (14) Jing and Geerts (2015) analyze the impact of seeding in stratiform and convective storms respectively, both over the Sierra Madre, and both using DOW reflectivity and dual-pol variables.
(15) Jing et al. (2015c) demonstrate a positive "downwind" (extra-area) effect, i.e. increased snowfall downwind of the target range.
(16) Chu et al. (2015) use WRF LES simulations to evaluate the seeding impact for a super-shallow layer cloud partially blocked by the terrain (13 Feb 2013).
(17) Geerts and Pokharel (2015) provide observational evidence for ice crystal generation by blowing snow in shallow orographic clouds.
(18) Rauber et al. (2015) survey historical progress in our understanding of the impact of glaciogenic seeding of orographic on precipitation, from the 1950s to ASCII.

Here are the full references:

Geerts, B. and co-authors, 2013: The AgI Seeding Cloud Impact Investigation (ASCII) campaign 2012: overview and preliminary results. *J. Wea. Mod.*, **45**, 24-43.

Miao, Q., and B. Geerts, 2013: Airborne measurements of the impact of ground-based glaciogenic cloud seeding on orographic precipitation. *Advances in Atmospheric Science*, **30**, 1025-1038. doi: 10.1007/s00376-012-2128-2. (link).

Boe, B., and co-authors, 2014: The dispersion of silver iodide particles from ground-based generators over complex terrain. Part I: Observations with acoustic ice nucleus counters. *J. Appl. Meteor. Climatol.*,**53**, 1325–1341.

Xue, L., X. Chu, R. Rasmussen, D. Breed, B. Boe, B. Geerts, 2014: The dispersion of silver iodide particles from ground-based. Part II: WRF Large-Eddy Simulations v.s. observations. *J. Appl. Meteor. Climatol.*, **53**, 940-958.

Pokharel, B., B. Geerts, and X. Jing, 2014a: The impact of ground-based glaciogenic seeding on orographic clouds and precipitation: a multi-sensor case study. *J. Appl. Meteor. Climat.*, **53**, 890-909. (21 Feb 2012 case study)

Pokharel, B., B. Geerts, X. Jing, K. Friedrich, J. Aikins, D. Breed, R. Rasmussen, and A. Huggins, 2014b: The impact of ground-based glaciogenic seeding on clouds and precipitation over mountains: a multi-sensor case study of shallow precipitating orographic cumuli. *Atmos. Res.*, **147**, 162-182. (13 Feb 2012 case study) http://dx.doi.org/10.1016/j.atmosres.2014.05.014

Pokharel, B., and B. Geerts, 2014: The impact of glaciogenic seeding on snowfall from shallow orographic clouds over the Medicine Bow Mountains in Wyoming. *J. Wea. Mod.* , **46**, 8-29. (link).

Chu, X., B. Geerts, L. Xue, and R. Rasmussen, 2014: Radar observations and WRF LES simulations of the impact of ground-based glaciogenic seeding effect on orographic clouds and precipitation: Part I: Observations and model validations. *J. Appl. Meteor. Climat.*, **53**, 2264-2286.

Geerts, B., Y. Yang, R. Rasmussen, S. Haimov, and B. Pokharel, 2015: Snow growth and transport patterns in orographic storms as estimated from airborne vertical-plane dual-Doppler radar data. *Mon. Wea. Rev.* , **143**, 644-665.

Jing, X., B. Geerts, K. Friedrich, and B. Pokharel, 2015: Dual-polarization radar data analysis of the impact of ground-based glaciogenic seeding on winter orographic clouds. Part I: mostly stratiform clouds *J. Appl. Meteor. Climat.*, accepted.

Pokharel, B., B. Geerts, and X. Jing, 2015a: The impact of ground-based glaciogenic seeding on clouds and precipitation over mountains: a case study of a shallow orographic cloud with large supercooled droplets. *J. Geophys. Res. Atmosphere*, accepted.

Jing, X., and B. Geerts, 2015: Dual-polarization radar data analysis of the impact of ground-based glaciogenic seeding on winter orographic clouds. Part II: convective clouds *J. Appl. Meteor. Climat.*, accepted.

Jing, X., B. Geerts, and B. Boe, 2015: The extra-area effect of orographic cloud seeding: observational evidence of precipitation enhancement downwind of the target mountain. *J. Appl. Meteor. Climat.*, in review.

Xue, L., X. Chu, R. Rasmussen, and D. Breed, and B. Geerts, 2015: A case study of radar observations and WRF LES simulations of the impact of ground-based glaciogenic seeding on orographic clouds and precipitation. Part II: AgI dispersion and seeding signals simulated by WRF. *J. Appl. Meteor. Climat.*, in review.

Pokharel, B., B. Geerts, X. Jing, K. Ikeda, and R. Rasmussen, 2015b: A multi-sensor study of the impact of ground-based glaciogenic seeding on clouds and precipitation over mountains in Wyoming in relation to ambient and cloud conditions. *J. Appl. Meteor. Climat.*, in preparation, submitted in early May.

Rauber, R. M., B. Geerts, L. Xue, J. French, K. Friedrich, R. Rasmussen, and S. Tessendorf, 2015: Wintertime orographic cloud seeding – a review. *J. Appl. Meteor. Climat.*, in preparation, submitted in early May.

Chu, X., B. Geerts, and L. Xue, 2015: A case study of radar observations and WRF LES simulations of the impact of ground-based glaciogenic seeding on a very shallow blocked orographic cloud. *J. Appl. Meteor. Climat.*, in preparation. (Presented at the AMS Annual meeting in Phoenix, Jan 2015)

Geerts, B. and B. Pokharel, 2015: Blowing snow as a natural glaciogenic cloud seeding mechanism. *Mon. Wea. Rev..*, in preparation (presented at the EGU meeting, Vienna, April 2015)

6. Presentations supported by the Grant

Dr. Geerts and his research group gave oral presentations at a series of meetings in all three years of the grant. These were partly funded by the NSF ASCII grant, partly by the UW Office of Water Programs grant.

a. <u>Weather Modification Association meetings</u>

2012: 44th Annual Meeting of the Weather Modification Association, in Las Vegas, 13-15 April 2012. Bart Geerts presented preliminary findings of the just-completed ASCII-12 campaign.

2013: 45th Annual Meeting of the Weather Modification Association, in San Antonio TX, 10-12 April 2013: Binod Pokharel presented an ASCII overview oral paper. Binod's trip was paid through an award he received (see below).

2014: 46th Annual Meeting of the Weather Modification Association, in Reno NV, 23-25 April 2014. Bart Geerts presented an ASCII overview oral paper, Binod Pokharel presented two posters (based on the papers Pokharel 2014a, and Pokharel et al. 2014b, listed above), and Xia Chu presented a poster based on Chu et al. (2014).

2015: 47th Annual Meeting of the Weather Modification Association, in Fargo ND, 22-24 April 2015. Bart Geerts presented the final ASCII overview (based on Pokharel et al. 2015b), Binod Pokharel presented a case study (3 March 2012), and Xia Chu presented a paper based on Chu et al. (2015).

b. <u>AMS Planned and Inadvertent Weather Modification meetings, and other AMS meetings</u>

- Bart Geerts gave a talk "The impact of AgI seeding on precipitation from orographic clouds: evidence from airborne profiling cloud radar data" at the 18th AMS Conference on Planned and Inadvertent Weather Modification, Seattle WA, 9-11 January 2011.
- A special session was devoted to ASCII at the American Meteorological Society 15th Conference on Mountain Meteorology in Steamboat Springs in Aug 2012 (**Fig. 2**) (http://ams.confex.com/ams/archives.cgi). Note that three oral presentations were given by graduate students funded by this grant and/or by the NSF ASCII grant, namely Binod Pokharel, Xia Chu, and Yang Yang.
- Xia Chu presented a poster "Validation of WRF and WRF LES Simulations of the Dispersal of Ground-generated AgI Nuclei" and Bart Geerts gave a talk "The ASCII 2012 campaign: overview and early results" at the 19th AMS Conference on Planned and Inadvertent Weather Modification, Austin, TX, 7-10 January 2013.
- Xia Chu presented a talk "case study of radar observations and WRF LES simulations of the impact of ground-based glaciogenic seeding on a very shallow blocked orographic cloud", Binod Pokharel gave a multi-sensor overview, and Bart Geerts gave a talk "The ASCII 2012 campaign: overview and lessons learned" at the 20th AMS Conference on Planned and Inadvertent Weather Modification, Phoenix AZ, 5-7 January 2015. We had two posters as well, one on DOW-based seeding impact assessment in ASCII (Xiaoqin Jing) and one on the 22 Feb 2012 case study (Binod Pokharel).
- Geerts was one of the panelists at a panel discussion on glaciogenic cloud seeding at the Phoenix AMS meeting. This discussion is summarized in a note in the *Bull. Amer. Meteor. Soc.* (Tessendorf et al., 2015)

3:45 PM-5:15 PM: Thursday, 23 August 2012

16 **Results from recent field campaigns: III**

Location: *Priest Creek C (The Steamboat Grand)*

Sponsor: ***15th Conference on Mountain Meteorology***

Papers:

3:45 PM 16.1 An overview of the ASCII 2012 (AgI Cloud Seeding Impact Investigation) campaign
***Bart Geerts**, University of Wyoming, Laramie, WY; and K. Friedrich, T. Deshler, D. A. R. Kristovich, J. Wurman, L. D. Oolman, S. J. Haimov, Q. Miao, D. W. Breed, R. Rasmussen, and B. A. Boe*

4:00 PM 16.2 Effects of atmospheric conditions and cloud seeding on orographic snowfall characteristics during the Silver Iodide (AgI) Seeding of Clouds Impact Investigation (ASCII) experiment
***Katja Friedrich**, University of Colorado at Boulder, Boulder, CO; and E. A. Kalina, B. Geerts, K. A. Kosiba, and J. M. Wurman*

4:15 PM 16.3 Using airborne vertical-plane dual-Doppler radar to analyze hydrometeor streamline patterns in orographic snow storms
***Yang Yang**, University of Wyoming, Laramie, WY; and B. Geerts*

4:30 PM 16.4 Airborne Cloud Radar and Lidar Observations of Blowing Snow during the ASCII Project: a Possible Natural Cloud Seeding Mechanism
***David A. R. Kristovich**, ISWS, Champaign, IL; and B. Geerts, Q. Miao, L. Stoecker, and J. M. Ritzman*

4:45 PM 16.5 Cold-season precipitation processes in shallow orographic clouds over a continental mountain range: impact of controlled ice nucleus injection
***Binod Pokharel**, University of Wyoming, Laramie, WY; and B. Geerts, Q. Miao, and K. Friedrich*

5:00 PM 16.6 Comparison of model and airborne measurement of AgI plumes from ground-based generators
*Lulin Xue, NCAR, Boulder, CO; and **X. Chu** and B. Geerts*

Fig. 2: List of oral presentations in the ASCII session at the 15th Conference on Mountain Meteorology in Steamboat Springs CO.

c. <u>Wyoming Weather Modification Pilot Project Technical Advisory Team meetings</u>

Bart Geerts presented ASCII research update at the bi-annual WWMPP Technical Advisory Team meetings in 2012, 2013, and 2014 (usually in Pinedale in July, and in Cheyenne in January). Bart Geerts also presented at the November "ground schools" for the WWMPP.

d. <u>Seminars</u>

Bart Geerts gave the following invited seminars:

- 2013/5/6: Dept. of Atmospheric and Environmental Sci., University at Albany ("Glaciogenic seeding of orographic clouds revisited")
- 2013/6/4: invited talk at NCAR, Boulder CO: "ASCII overview, key findings, and lessons learned" (this was a planning meeting to prepare for a new, larger NSF proposal following up on ASCII)
- 2013/6/13: invited presentation at the National Institutes for Water Resources (NIWR) annual meeting, South Tahoe CA: "Impact of glaciogenic cloud seeding on mountain snowfall: an old question revisited."
- 2013/11/6: Cocorahs webinar on glaciogenic cloud seeding , total full-time attendees: 87 (available at http://youtu.be/Br8W0sf3bdM)

- 2014/4/16: Enhanced water recovery from clouds: is it possible? University of Wyoming Spring 2014 Faculty Senate Award Speech, in Laramie
- 2014/4/22: Enhanced water recovery from clouds: is it possible? University of Wyoming Spring 2014 Faculty Senate Award Speech, in Casper
- 2014/11/25: ASCII overview, results, and lessons learned: a presentation at the Denver office of the Bureau of Reclamation.

7. Media coverage

In Year 2 Geerts' research was covered in the Laramie Boomerang, the Casper Star Tribune, the Wyoming Business Chronicle, and the University of Wyoming News (http://www.uwyo.edu/uw/news/). The Associated Press had an article on 5/1/2014, and several news outlets carried the article, upon which Geerts was interviewed by ClimateWire in Washington, D.C. We were also part of the Weather Channel's "Hacking the Planet" series in early April 2013. The episode in which we are featured can be viewed at http://youtu.be/rVl_pjEOi9w (this is one of several episodes in the Hacking the Planet series). Note that this is an unlisted and unlinked video, i.e. it is *not* public – the only way to access it is through this link. The reason, of course, is copyright issues.

8. Dissertations/theses

Three MSc theses were partly or entirely funded by this grant:
- Ms. Yang Yang has been partly supported by the current and a previous UW Office of Water programs grant. She defended her thesis "Snow transport patterns in orographic storms as estimated from airborne vertical-plane dual-Doppler radar data" on 23 May 2013, and officially graduated in Fall 2013.
- Ms. Xia Chu defended her thesis "Cloud-resolving Large Eddy Simulations of the impact of AgI nuclei dispersed from the ground on orographic clouds and precipitation: model validation" on 6 June 2013, and officially graduated in Summer 2013.
- Ms. Xiaoqin Jing defended her thesis "Dual-polarization radar data analysis of the impact of ground-based glaciogenic seeding on winter orographic clouds" on 18 August 2014, and officially graduated in Summer 2014.

Two PhD dissertations were partly or entirely funded by this grant:
- Dr. Binod Pokharel (PhD) "A Multi-Sensor Study of the Impact of Ground-Based Glaciogenic Seeding on Orographic Clouds and Precipitation." (graduated in Dec 2014)
- Ms. Xia Chu (PhD) hopes to defend her dissertation by May 2016.

9. Awards

- Graduate student Binod Pokharel, who has been partly funded by this grant, received the 2012 North American Interstate Weather Modification Council Student Award. This is a $1000 fellowship plus all travel expenses to the WMA annual meeting, in 2013 in San Antonio TX, where Binod gave a presentation.

- Bart Geerts received the 2012 National Institutes of Water Resources (NIWR) "IMPACT" Award to the PI (Dr. Geerts), a national recognition initiated by the UW Office of Water Programs. He received the award at the NIWR meeting in Tahoe CA in June 2013.
- Graduate student Xia Chu received an NCAR Advanced Studies Program (ASP) doctoral fellowship (host: Lulin Xue), partially funded by the UW Office of Water Programs. She is spending the full year 2015 in Boulder CO.
- Bart Geerts received the Spring 2014 UW Faculty Senate Award. He gave presentations on weather modification at the UW campuses in Laramie and Casper WY, for which he received a $1000 honorarium.

Decadal Scale Estimates of Forest Water Yield After Bark Beetle Epidemics in Southern Wyoming

Basic Information

Title:	Decadal Scale Estimates of Forest Water Yield After Bark Beetle Epidemics in Southern Wyoming
Project Number:	2012WY82B
Start Date:	3/1/2012
End Date:	2/28/2015
Funding Source:	104B
Congressional District:	1
Research Category:	Climate and Hydrologic Processes
Focus Category:	Hydrology, Surface Water, Water Quantity
Descriptors:	None
Principal Investigators:	Brent E. Ewers, Urszula Norton, Elise Pendall, Ramesh Sivanpillai

Publications

1. Ewers, BE., 2013. Understanding Stomatal Conductance Responses to Long-Term Environmental Changes: A Bayesian Framework that Combines Patterns and Processes. Tree Physiology. 33:119-122.
2. Schlaepfer, DR, BE Ewers, BN Shuman, DG Williams, JM Frank, WJ Massman, WK Lauenroth., 2014. Terrestrial water fluxes dominated by transpiration: Comment Arising from S. Jasechko et al. Nature 496:357-351 (2013).
3. Biederman, J, A Harpold, D Gochis, BE Ewers, D Reed, S Papuga, P Brooks., 2014. Compensatory vapor flux reduces water for streamflow following severe bark beetle-induced forest mortality. Water Resources Research 50(7):5395-5409.
4. Frank, JM, WD Massman, BE Ewers, L Huckabee, J Negron., 2014. Ecosystem CO2/H2O fluxes are explained by hydraulically limited gas exchange during tree mortality from spruce beetles. Journal of Geophysical Research-Biogeosciences. 119:1195-1215.
5. Norton, N, BE Ewers, B Borkhuu, E Pendall., 2015. Soil and litter nitrogen and greenhouse gas fluxes during five years of bark beetle infestation in a lodgepole pine forest. Soil Science Society of America Journal 79(1):282-293.
6. Reed, D, BE Ewers, E Pendall., 2014. Impact of mountain pine beetle induced mortality on forest carbon and water fluxes. Environmental Research Letters. 9:105004. Doi:10.1088/1748-9326/9/10/105004.
7. Schlaepfer, DR, BE Ewers, BN Shuman, DG Williams, JM Frank, WJ Massman, WK Lauenroth., 2014. Terrestrial water fluxes dominated by transpiration: Comment. Ecosphere. 5:art61. Doi: 10.1890/ES13-00391.1.
8. Borkhuu, Bujadma, 2014. Aboveground and belowground carbon cycle responses to bark beetle infestation in a lodgepole pine forest, Ph.D. Dissertation, University of Wyoming, Botany, December, 105 pgs.
9. Reed, David, 2014. Observing and diagnosing biological fluxes and canopy mechanisms with implications for climate change and ecosystem disturbance, Ph.D. Dissertation, University of Wyoming, Botany, May, 168 pgs.

Decadal Scale Estimates of Forest Water Yield After Bark Beetle Epidemics in Southern Wyoming

PIs Brent E Ewers, Elise Pendall, Urszula Norton, Ramesh Sivanpillai

Final Report

Abstract

The forests in Wyoming are undergoing profound changes in their hydrologic partitioning of precipitation due to an ongoing epidemic of bark beetles. These forests are key components of major river watersheds and could magnify any impacts on downstream users of water. Recent research at the forest stand scale has shown that while the trees die over the first several years of an outbreak, evapotranspiration declines, soil moisture increases, soil nitrogen increases and snowpack increases and melts faster. These changes in forest hydrology strongly suggest that streamflow should increase. However, ongoing streamflow measurements show no increase. This conundrum between stand processes and watershed processes was directly addressed by this project. Further, the length of time in which hydrological changes at the stand scale will persist is unknown because of lack of knowledge about how these stands will experience succession during and after bark beetle epidemics. To address these issues we 1) quantified tree, seedling, sapling and other understory species composition in forest stands to characterize succession and 2) utilized multiple remote sensing tools to improve scaling between well-instrumented forest stands and watersheds. In addition to these two objectives we will synthesize a large amount of prior and ongoing data collection into an explicit data informatics framework. This framework will serve two purposes 1) novel data syntheses can occur in near real-time, enabling model-data fusion to improve predictions of streamflow and 2) rapidly serve data and model results for public and land manager use. This project builds on previous work that quantified and predicted water yield from bark beetle infested stands in the first five years of an outbreak and extends the time frame of predictions out to multi-decades. This work will enable both State and Federal water managers to make crucial predictions of streamflow from infested mountain ranges on time-frames that are relevant to land management decisions.

Objectives

1) Establish a web service for public and water management use that will provide direct access to data and model predictions

2) Predict the impact of forest succession from lodgepole and spruce-fir forests after bark beetle mortality on forest water yield and nitrogen loss from stands

3) Use ongoing stand and catchment scale measurements with remote sensing tools and mechanistic models to estimate bark beetle impacts on water yield at the mountain range scale

Methodology

We adopted the Terrestrial Regional Ecosystem Exchange Simulator-Cavitation (TREESCav) model for all the simulations for this project. The TREESCav model has the appropriate tree hydraulic and photosynthesis mechanisms to simulate bark beetle attacks. The model also has a full water budget including snow melt, sublimation, interception, soil moisture, drainage, tree transpiration and evaporation. The model includes Bayesian model-data fusion so that parameterization rigorously uses data. The hydrology community has begun to recognize that simulation of water budgets from vegetated watersheds must include carbon and nitrogen cycles for mechanistic and thus predictive understanding. Such an approach is necessary when projecting forest changes after a disturbance because carbon and nitrogen cycling co-limit forest production along with water. Thus, we have implemented new algorithms of soil carbon and nitrogen processing that can be compared to soil measurements of both processes from a recently finished NSF grant. This project supplied ongoing measurements of soil carbon and nitrogen pools and fluxes to constrain TREESCav as succession continues.

Our remote sensing approach utilizes Modis data as an appropriate compromise between spatial and temporal resolution based on preliminary analyses comparing the data to MODIS, Landsat and Aerocam.

The testing of both the TREESCav model and remote sensing data sets requires multiple data sets interacting at various temporal and spatial scales. To facilitate these comparisons and prepare the data for public sharing, we adopted Structured Query Language (SQL) approaches. We implemented SQL databases for all of the vegetation data from the Chimney Park and GLEES research sites which was funded by a grant from this agency that ended in Feb. 2013 (see final report for details). The database for the stand level fluxes, water budgets and vegetation are now completed. We have also finished the work with UW IT to allow serving of data. The spatial interface for querying data became available July 1, 2014 at http://wycehg.wygisc.org/. Analyses of downloaded data shows that members of state government have accessed the data. Work from this project provided the initial conceptualizations and seed money to start the server; it is now sustained by the Wyoming Center for Environmental Hydrology and Geophysics (WyCEHG).

Principal Findings (Cited Papers are in Publications Section)

Remote sensing of Leaf Area Index (LAI) shows that the footprint scale of the eddy covariance can be successfully analyzed with MODIS data during the mortality event (Figures 1 and 2). The bark beetle effect on basal area and leaf area occurs within a few years and is reflected at the individual stands as increased water filled pore space of soils, all of which is over within 3-5 years (Figures 3-4). This is less than half the time expected prior to collecting the data. We built a quantified response of water budgets to bark beetles over the first three years of the mortality event and found no increase in streamflow (Figure 5). Surprisingly, our results show that streamflow, when normalized by annual precipitation, actually decreases as mortality increases in contrast to hypotheses and some other watershed data. Our explanation for this difference includes the following components 1) forest succession is happening faster than expected and while the trees are dying, 2) the morality of 80% is not consistent within the flux tower footprint or watersheds, some patches are higher or lower, 3) the timing of each patch of mortality is not synchronized so that when one patch is at peak mortality (2-3 years), other patches that were attacked earlier are already recovering. In fact, studies of bark beetle infestation rates in watersheds show an average of 5-7 years to reach maximum mortality supporting our contention.

Moreover, the relationship between carbon and water exchange does not change (Figure 6) and even the long term stand-scale data set at GLEES only shows one year that is different in this relationship during the height of the beetle epidemic (Figure 7). Fine roots play a key role in these responses (Figure 8) and suggest that root dynamics need to be included in our model work, which we incorporated into TREESCav in the past six months.

Objectives two and three required successful testing of the TREESCav model against the bark beetle mortality datasets from the Chimney Park and GLEES research sites. The Bayesian approach to model parameterization via fusion with data is superior for processes that have uncertainty in both the processes and data (Ewers et al 2013). With this conceptual framework in place, we have tested the model against tree transpiration, evapotranspiration, tree hydraulic and tree nonstructural carbohydrates and total net ecosystem exchange of CO2. The model has been very successful in simultaneously simulating all of these processes except for one (see next paragraph). Our Bayesian model-data fusion analyses now show that the model is simulating the data as best as possible at the individual tree level given the uncertainties in the data itself . We were only able to simulate these fluxes successfully when appropriate root and microbial response to soil moisture and nitrogen were included showing the link to stand water budgets and water quality. The resulting posterior distribution of major parameters after testing the model against data is shown in Figure 9. The effort required to obtain these results has been significant in both coding and processing time. With the help of Jared Baker from UW-ARCC, TREESCAv is now running on Mt Moran HPC reducing the time to run a full Bayesian simulation of one year from 10 days to 8 hours. Using this improvement in simulation time, we have made longer term estimates of ecosystem water and carbon fluxes beyond 10 years.

An unexpected finding from our work is the enormous amount of water vapor fluxes that occur during the winter (Figure 10). The relationships between SWE and runoff is not altered by bark beetles (Figures 11 and 12) providing another empirical data set supporting lack of bark beetle impacts. If we run TREESCav using incoming snow fall, the model is only able to simulate about 25% of this winter water vapor flux from snow. Other models that rely on a basic snow energy balance perform just as poorly. We now have a new water vapor isotope laser purchased using NSF EPSCOR funds (a project that was funded partially due to previous funding from this agency). This laser allows partitioning of water vapor fluxes every half hour during the entire year. Thus, we can determine when water vapor flux is occurring from snow in either the pack or the canopy with little liquid water present (sublimation). We will formulate a mechanistic snow sublimation submodel in TREESCav to appropriately simulate these enormous winter water vapor fluxes.

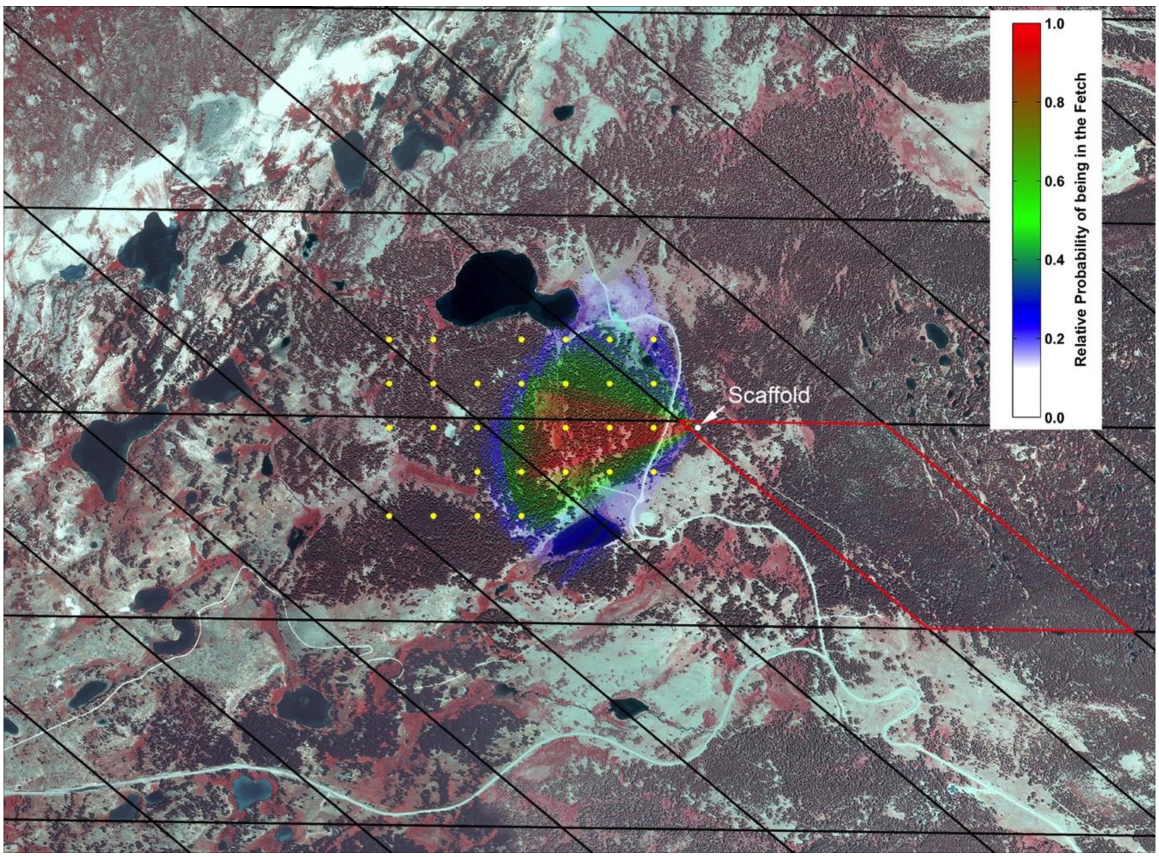

Figure 1. MODIS scene of the GLEES area showing the location of the scaffold holding the eddy covariance, micrometerological and isotope laser instruments. The colors are the relative probability of the flow footprint of the tower, which is mostly spruce and fir forest undergoing back beetle mortality. The red trapezoid to the SE of the tower was used to quantify the change in land cover over time because it is nearly all forest with no lakes. From Frank et al. 2014.

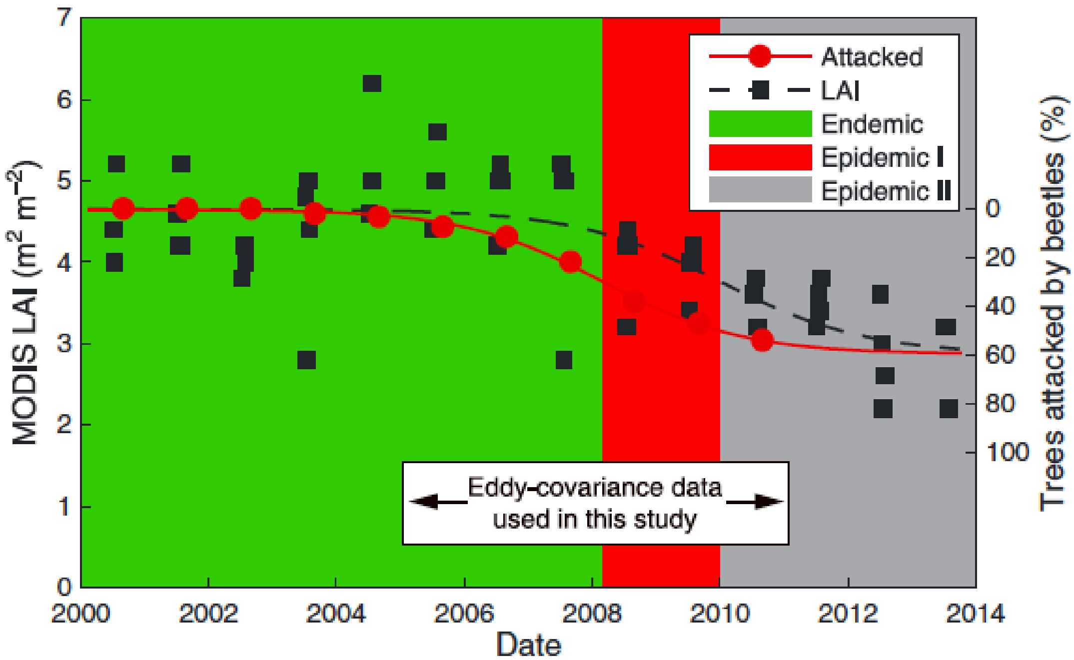

Figure 2. Time series of MODIS LAI estimated from the pixel identified in Figure 1. The data clear shows that LAI changes lag the timing of attack by beetles by about two years. From Frank et al 2014.

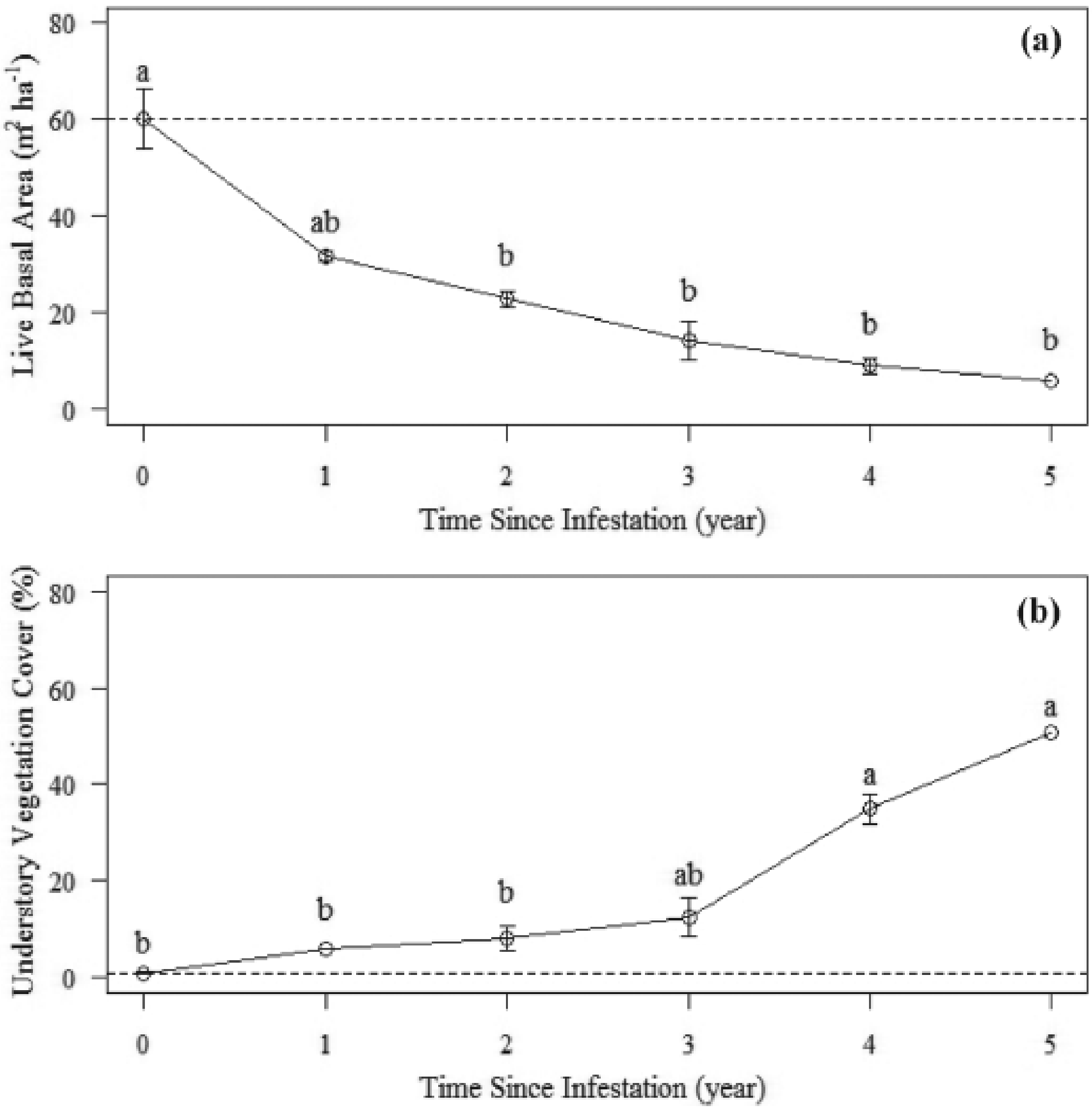

Figure 3. Effects of the beetle infestation on (a) Live Basal Area and b) understory vegetation cover as a function of time since infestation (year) in lodgepole pine forest, southeastern Wyoming. From Norton et al 2015.

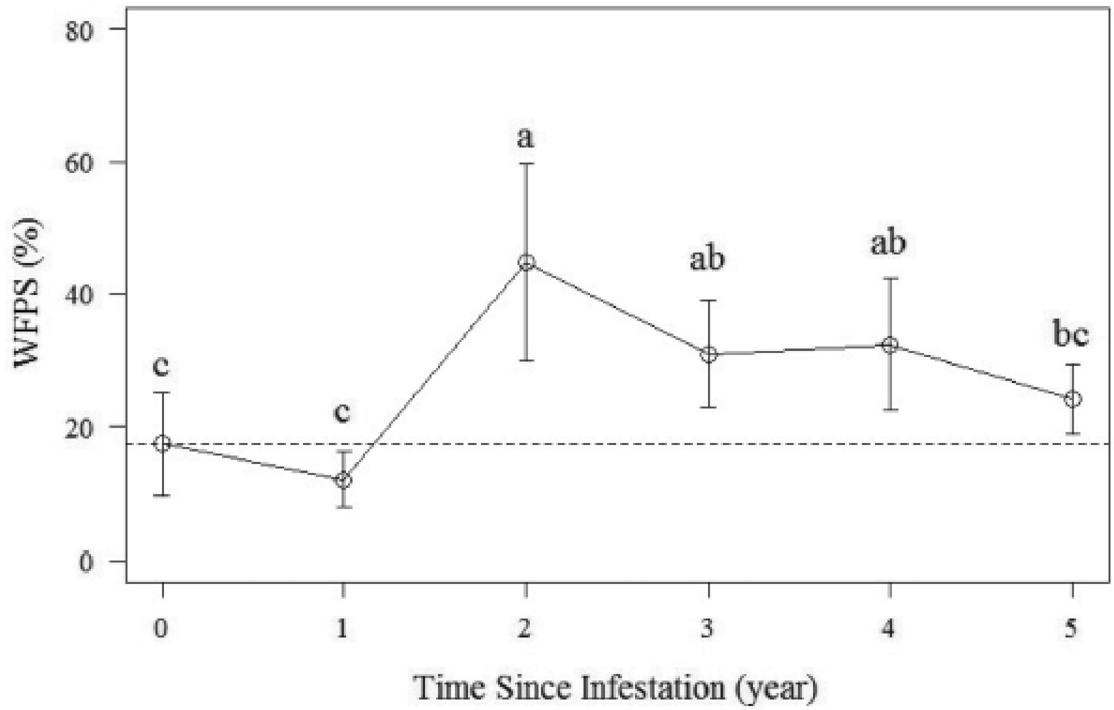

Figure 4. Effects of the beetle infestation on water filled poor space (WFPS). The bark beetle impact occurs within two years and is gone quickly within 3 to 5 years. From Norton et al 2015.

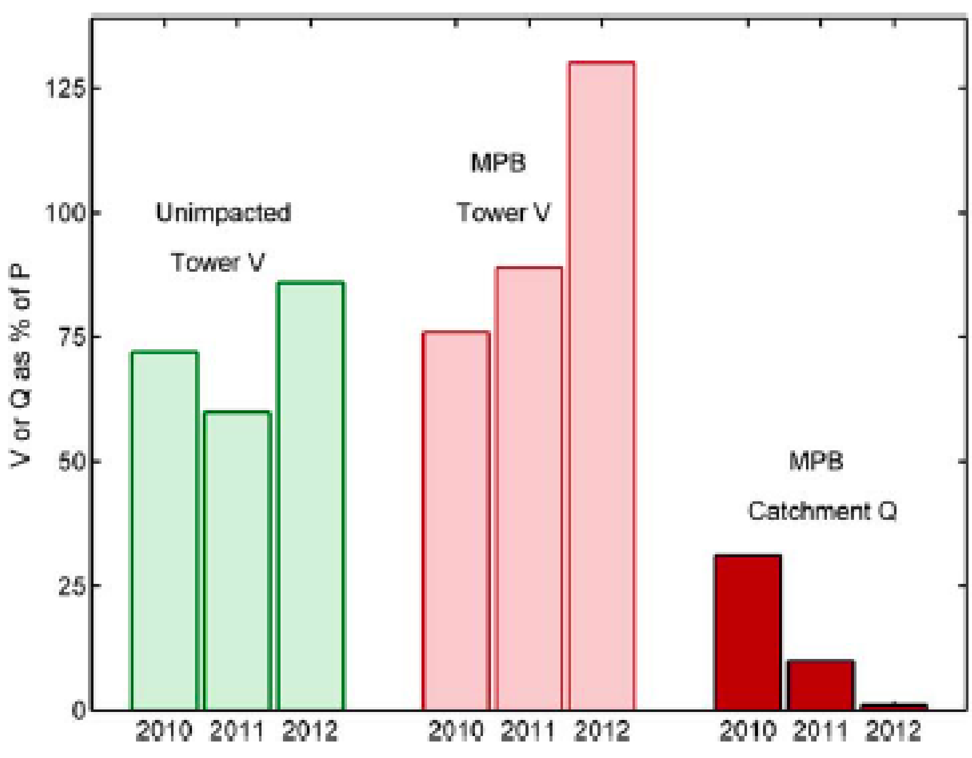

Figure 5. Annual observation of hydrologic paritioning to vapor loss V and streamflow Q expressed as a percentage of precipitation P (i.e. V: P = vapor loss coefficient and Q: P = runoff coefficient). Partitioning was less variable at the Unimpacted site and followed the pattern of interannual climate, with V: P inversely related to annual P (Table 3). The MPB site showed greater partitioning and less to Q in 2011 as compared to 2010 in spite of larger P. In 2012, which was very dry at the MPB site, tower V exceeded P, in part due to a release of stored water, and very little Q was observed. From Biederman et al In 2014.

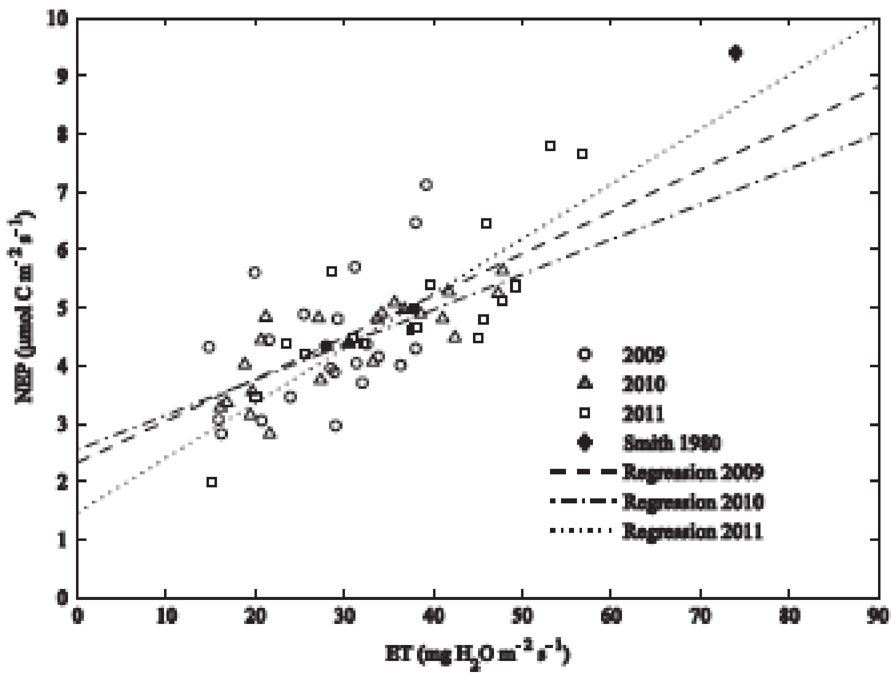

Figure 6. Relationship between Net Ecosystem Productivity (NEP-net storage of CO2 into the forest) and evapotranspiration (ET) over a lodgepole pine forest. There is no statistical difference in this relationship as bark beetle mortality increases from 30% in 2009 to 75% in 2011 indicating that mortality does not impact water use efficiency of CO2 uptake. From Reed et al 2014.

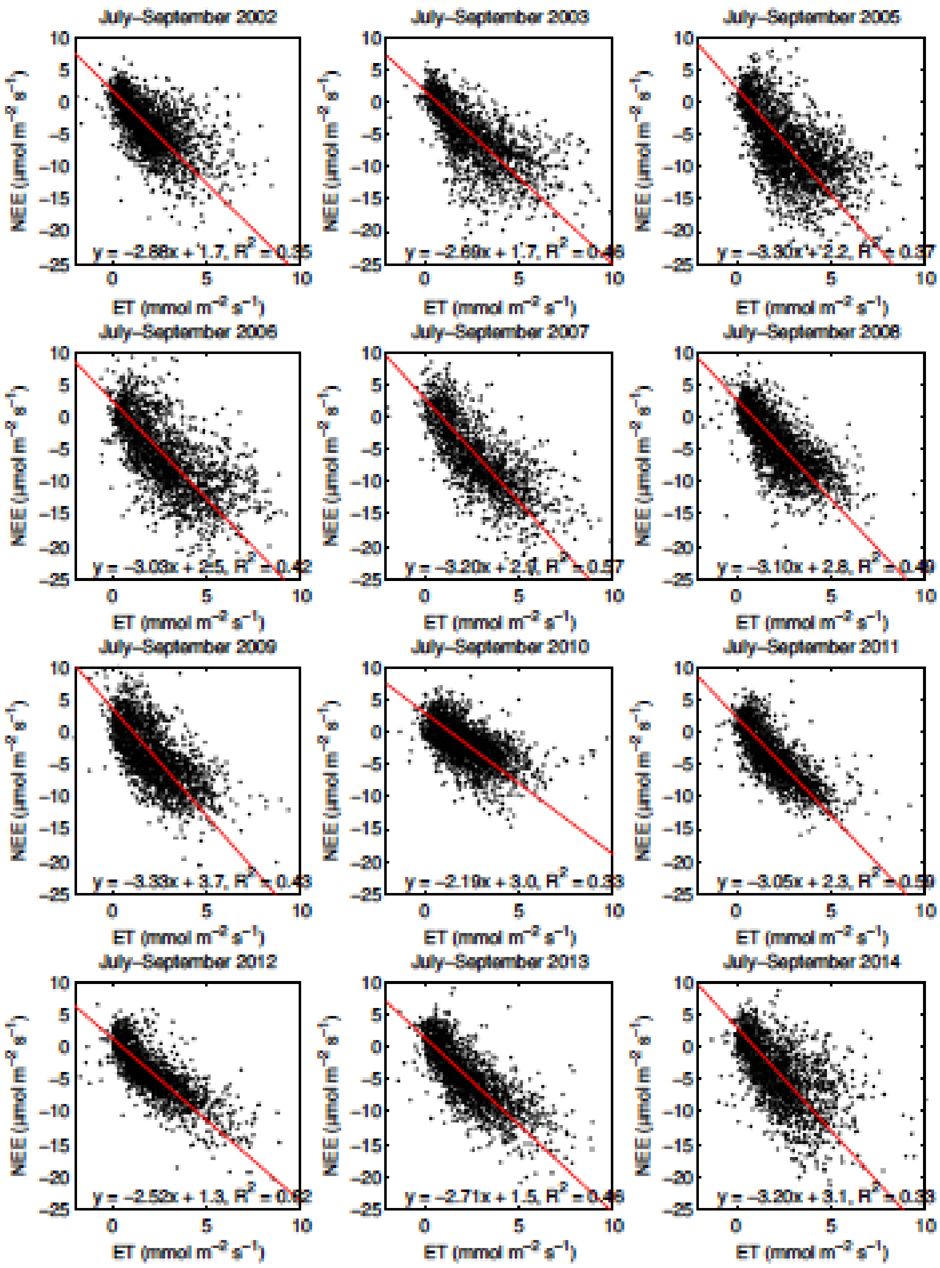

Figure 7. Relationships between net ecosystem exchange of CO2 (NEE) and evapotranspiration (ET) over a spruce-fir forest. Bark beetle mortality started in 2008 and reached it's peak in 2010 (see Figure 2). The relationship between NEE and ET showed a lower ET loss in 2008 and 2009 and lower NEE and ET in 2010. Both NEE and ET were back to pre beetle levels a year later in 2011 and have stayed as high through 2014. Frank et al In Preparation.

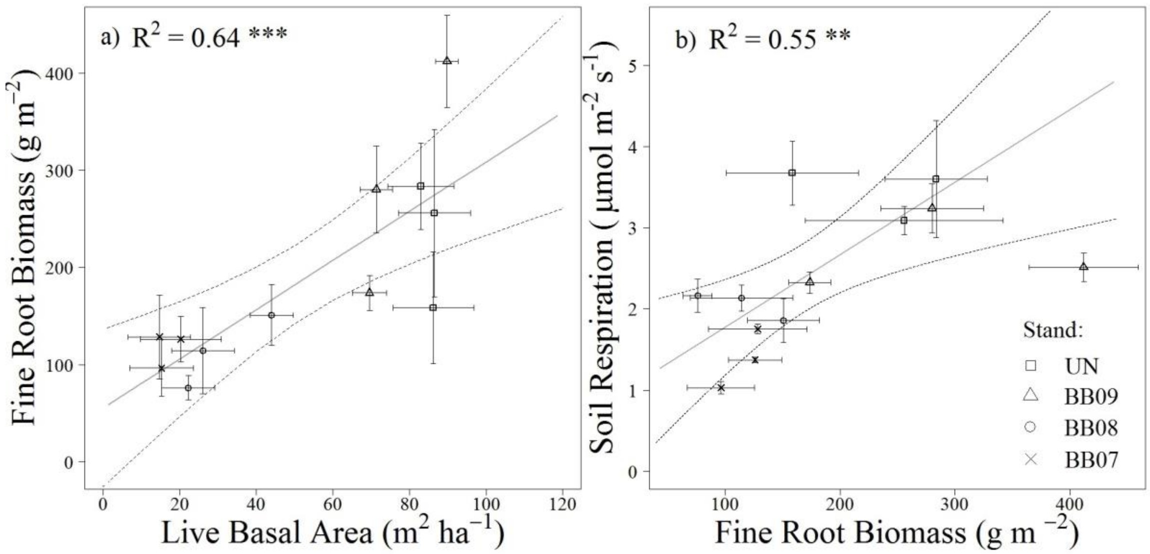

Figure 8. Relationships between live basal area and fine root biomass and fine root biomass and soil respiration across four stands of lodgepole pine that were invested in 2007, 2008 or 2009 measured three to five years later. The relationships indicate that loss of living tree impacts carbon fluxes at the stand scale but these response is muted at the forest scale (Figure 6). From Borkhuu et al Accepted.

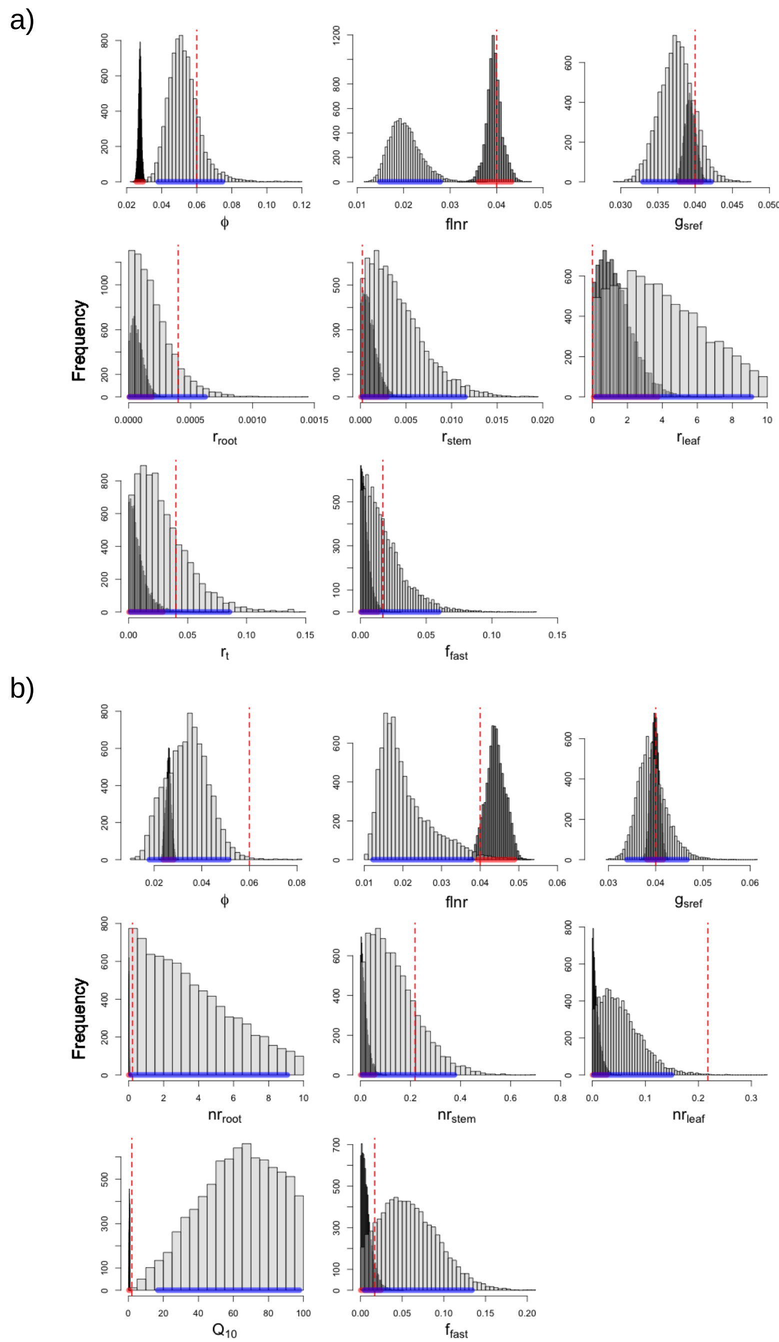

Figure 9. Posterior distributions for TREESCav to test the model ability to simulate the CO2 exchange of the forest based on the data from Figures 6 and 7. The two sets of parameters in (a) and (b) are from a parsimony analysis that supports the parameterization in (a) more. Parameter distributions from hourly aggregation are shown in darker grey with 95% credible intervals highlighted in red, while distributions from daily aggregation are shown in lighter grey with 95% credible intervals highlighted in blue. Overlap in 95% credible intervals is displayed in purple. Parameter values taken from literature or measured are shown with a red dashed vertical line. The parameters include the major carbon, water and nitrogen cycling components in the TREES model. Gsref is most

relevant to evapotranspiration because it is the total canopy conductance that is responding to the mortality event. From Peckham et al In Review.

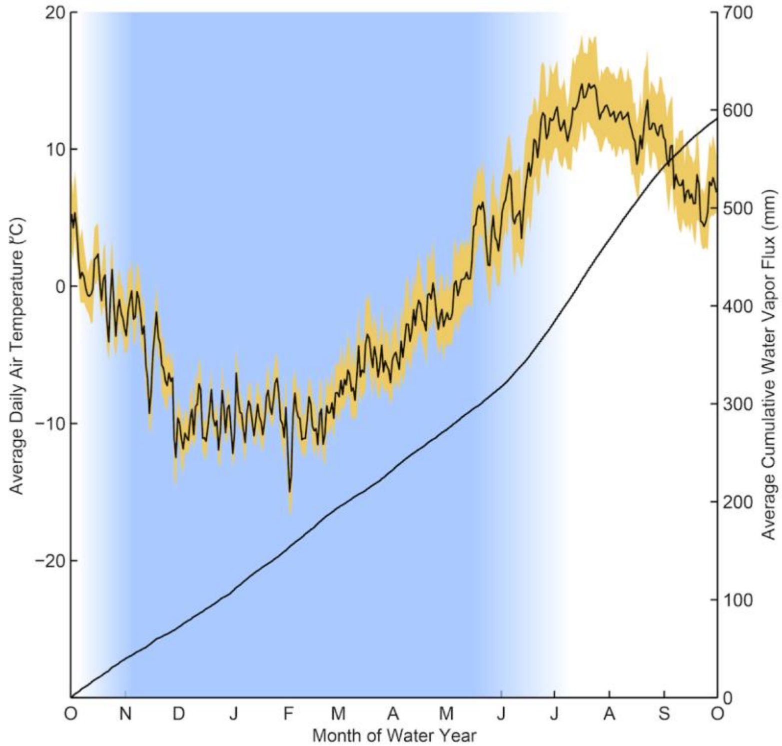

Figure 10. Average cumulative water vapor flux (solid line) for the past eight years at GLEES. The snowpack persists for an average of eight months per year (blue shading) while the climate is below freezing a majority of that time (lines with yellow shading: average daily minimum, mean, and maximum air temperatures). Sublimation accounts on average for 50 +/- 10% (SD among years) of the total annual water vapor flux. From Schaepfer et al 2014.

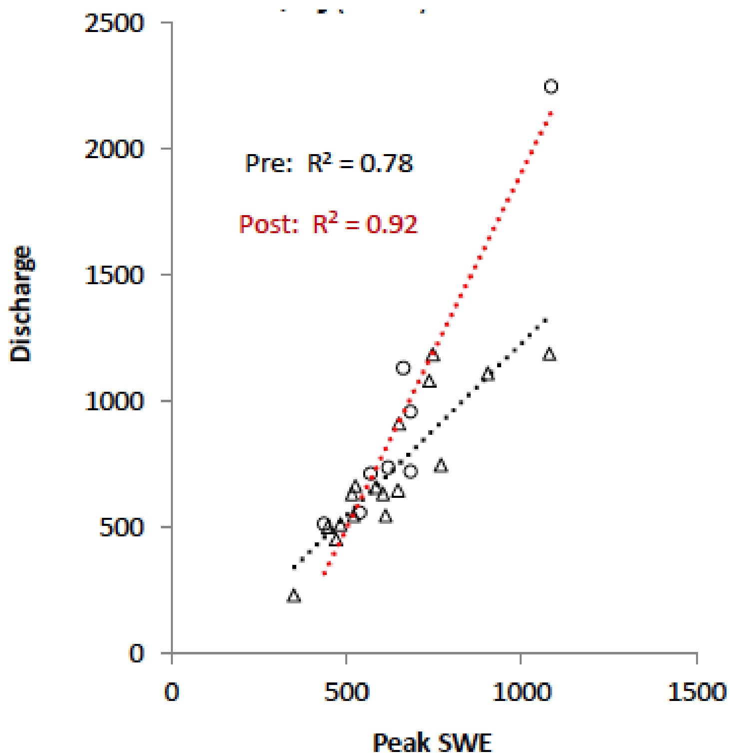

Figure 11. Discharge vs Peak Snow Water Equivalent from the Little Laramie Watershed from 1989-2013. There was no statistical difference in the pre and post-bark beetle relationship. From Hyde et al In Prep.

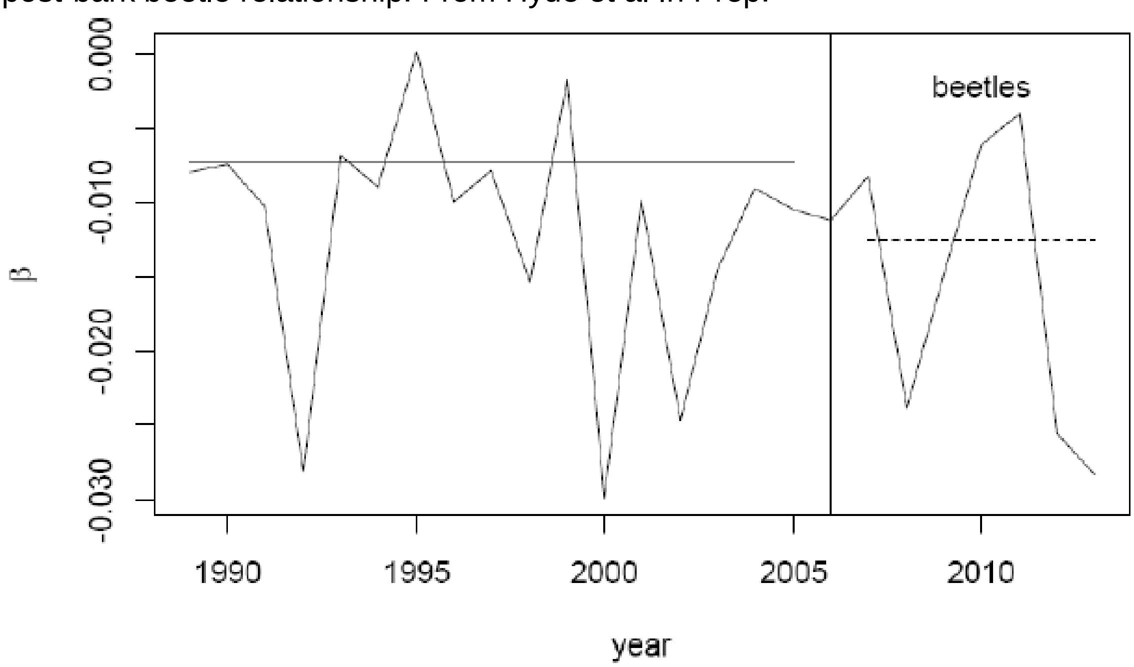

Figure 12. Analyses of the slope (Beta) vs water year for the Little Laramie Watershed from 1989-2013 (same as Figure 11). No statistical difference was found after bark beetle mortality in the response of discharge to SWE. These analyses suggest that the mechanism that prevent increased streamflow at the individual watershed scale (Figure 5) also occur at the mountain range scale.

Thus, we expect that successful TREESCav predictions of watershed should translate to the mountain range. From Hyde et al In Prep.

Once the stand scale analyses are complete, we will run the model at the watershed and mountain range scale using Landsat data sets tested against ground data. The Landsat analyses are funded by the Wyoming Weather Modification Project. Ongoing analyses of this data have shown that dead trees are well correlated to several individual spectral bands and indices. However, no spectral analyses have been able to distinguish between spruce/fir and lodgepole pine dead trees so we are adding ancillary data on slope, aspect and elevation to produce final maps. The stand-scale version of TREESCav will then be run at the watershed and landscape/mountain range scale using these final maps.

Simulating the impact of tree mortality at decadal scales required continued refinement of the soil carbon and nitrogen processes and the implementation of a canopy competition and root expansion algorithms in TREESCav. We know have data from 3-4 years of recovery in some stands which shows a dramatic increase in understory vegetation including tree saplings and seedlings as well as increased nitrogen and loss in soils. We have now run TREESCav over many years (Figure 13), but the model overestimates the beetle mortality impact (Figures 14-15). Our model analyses show that TREESCav misses these vegetation and thus hydrology dynamics unless soil nitrogen processes, light competition and root dynamics are appropriately captured. Our model results provide another piece of evidence that bark beetles do not increase streamflow because including the bark beetle effect on individual trees without appropriate compensating mechanisms dramatically underestimates ET and thus overestimates streamflow. This problem is common to all model studies without appropriate feedbacks during and after the mortality event.

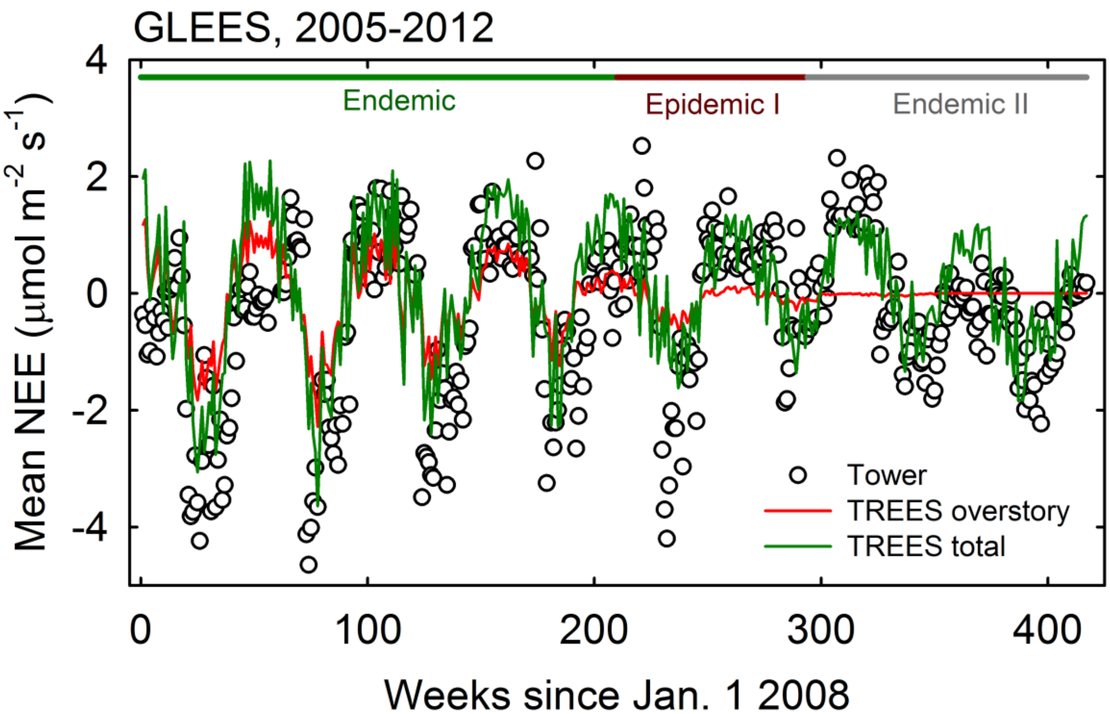

Figure 13. TREESCav simulations of net ecosystem exchange of CO2 using an algorithm of canopy competition. Notice that during the prior to the beetle mortality (Endemic) the fluxes are similar for overstory and total because the large trees outcompete the understory. When the overstory dies in Epidemic I and the understory begins to recover in Epidemic II, the competition shifts more to non-trees (see flat red line) but TREEScav still capture the overall CO2 fluxes. CO2 fluxes are an appropriate first testing phase of this algorithm because total ecosystem photosynthesis must be appropriately simulated with respect to competition before we can expect to successfully simulate ET and waterbudgets.

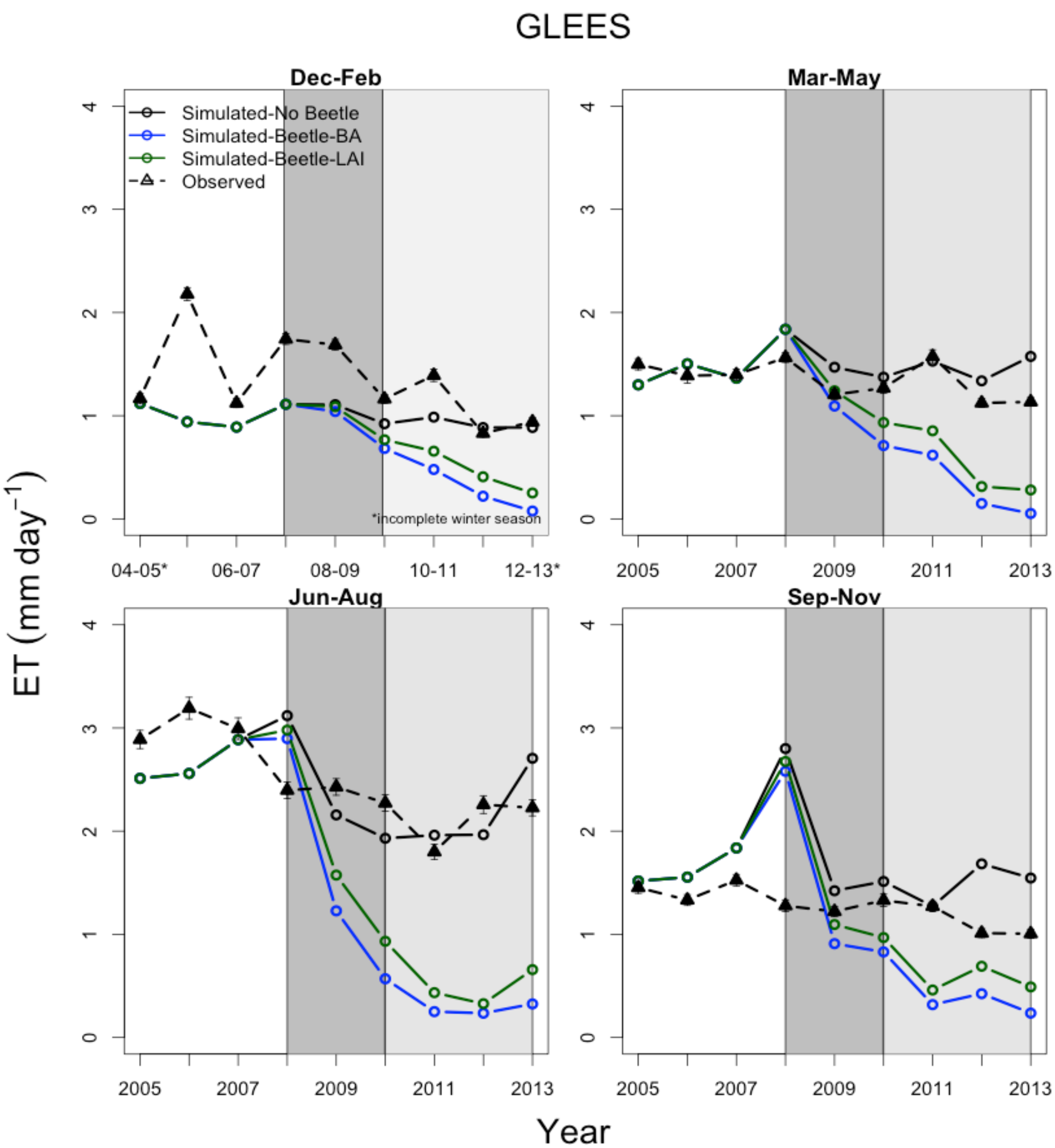

Figure 14. TREESCav simulations of evapotranspiration (ET) showing systemic overestimation of the beetle effect during (dark gray) and after (light gray) the mortality event. Millar et al In Preparation.

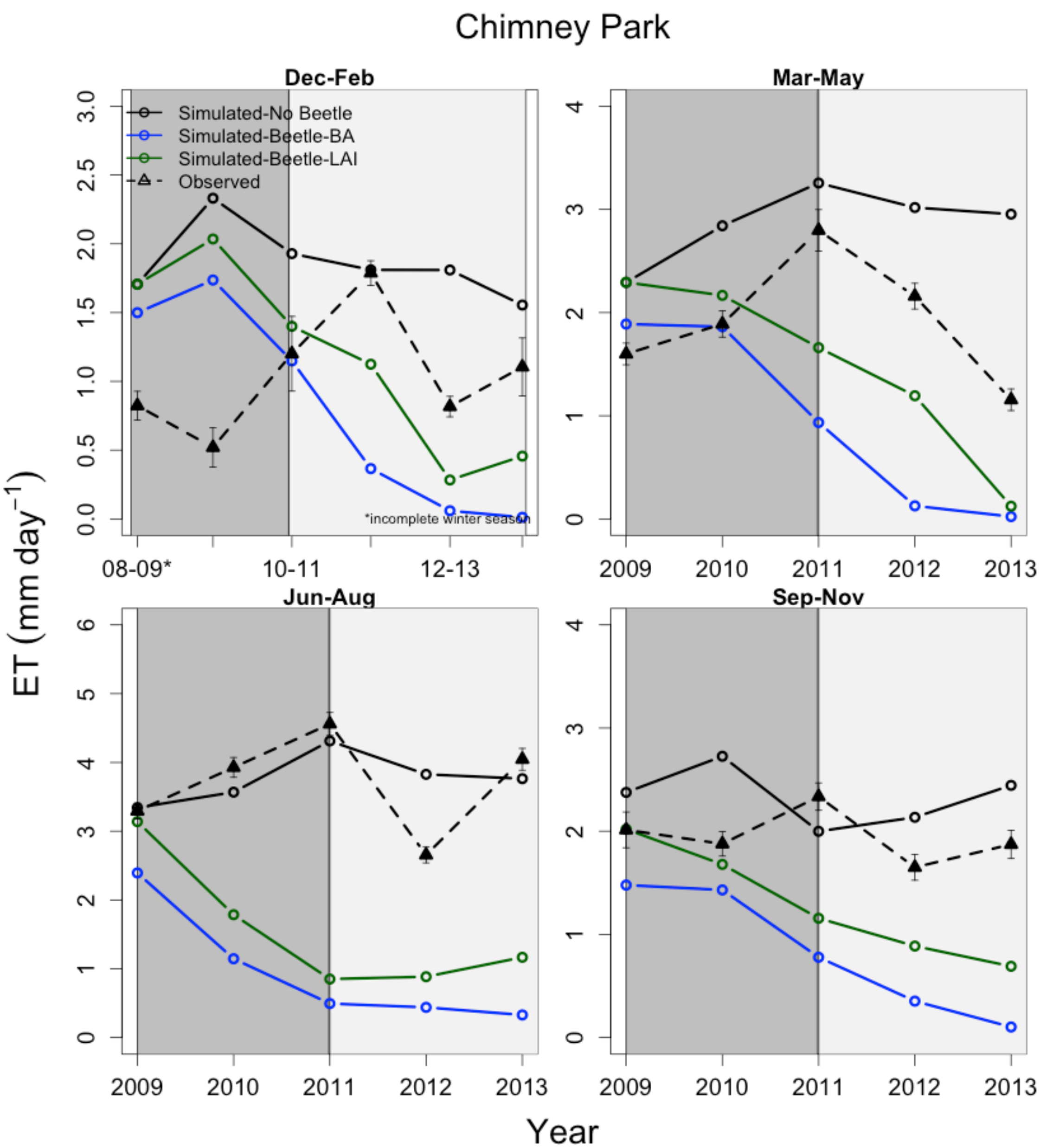

Figure 15. Figure 7 TREESCav simulations of evapotranspiration (ET) showing systemic overestimation of the beetle effect during (dark gray) and after (light gray) the mortality event. Millar et al In Preparation.

Significance

Many studies over the past 10 years have documented increased mortality of forests globally. However, none of these studies have truly mechanistic connections between tree mortality and larger scale consequences such as water yield and quality. Our study is making these connections by rigorously testing a simulation model with stand data from two different forests in Wyoming experiencing mortality from bark beetles. By starting with the stand-scale of data and incorporating carbon and nitrogen cycling, we have much more confidence when we infer changes at larger spatial scales in watersheds and landscapes/mountain ranges and longer temporal scales as the forests recover from the disturbance.

Surprisingly, we found relatively little impact of the mortality event on watershed responses due to the spatial and temporal patchiness of the mortality and the fast recovery of the individual patches. These spatial and temporal scaling issues provides an explanation for why our results are different from many other studies that focus on forested watersheds that have more uniform mortality or simulate mortality as uniform. At the very least, our results suggests extreme caution should be taken when simulation models assume that bark beetle remove tree transpiration in the same manner as clearcutting or fires.

We also found that winter water vapor fluxes (nominally snow sublimation) were an enormous component of total annual water vapor fluxes. These large winter water vapor fluxes cannot be simulated by any model, so future work is developing a new snow sublimation model for TREESCAv. These large winter water vapor fluxes also suggest that water managers can not just use incoming snow to predict streamflow in any mechanistic manner. These results also have implications for the Wyoming Weather Modification Project because the small potential increases in snowfall predicted by that project may be offset by sublimation.

Our serving of data from this project enables policy implications to occur faster. Any policy maker who disagrees with our interpretation of the data is free to download all the data presented in this report and conduct their own analyses. We have leveraged funds from the WyCEHG project (see leveraged funding below) to support this distribution of data with links to other relevant water projects around southern Wyoming.

Students/Post-Docs Supported

Bujidma Borkhuu- PhD student finished December 2014, main responsibilities were soil measurements and assistance with atmospheric measurements. Received partial funding from this project.

Stan Devore- undergraduate student doing lab processing of field samples, plans to graduate in Spring 2016

Bridger Huhn- undergraduate student doing lab processing of field samples, plans to graduate in Spring 2016

Ben Ingold- undergraduate student collecting field samples, graduated Spring 2014 currently employed as field technician for USFS

Kaleb Kenneaster-undergraduate student doing lab processing of field samples, enrolled in WWAMI program for medical school

Andrew King-ongoing MS student, main responsibilities are remote sensing image analysis and comparison to vegetation databases established through this project. Receives partial funding from this project.

Nick Brown-ongoing MS student, main responsibilies are soil measurements of nitrogen and carbon cycles. Receives partial funding from this project.

John Frank- ongoing PhD student, main responsibilities are all of the flux measurements from the spruce and fir bark beetle site (note: John Frank is a full time employee of the USFS RM Exp St in Ft. Collins, and does not receive any salary support from this project). Support from this project is used for field visits and site maintenance through a USFS subcontract.

David Reed-PhD student finished May 2014, main responsibilities were the atmospheric and streamflow measurements. Received partial funding from this project. David received a position as a visiting assistant professor at Dickinson College and obtained an NSF post-doc fellowship to work at the University of Wisconsin-Madison startin in May, 2015.

Scott Peckham- post-doctoral scientist, main responsibilities were coding modifications to the TREES model and model-data fusion analyses as well as supervision of the Chimney Park lodgeople pine site. Received full support from this project. Dr. Peckham is a big game ecologist for the USFS in Oregon.

Publications (*Students and Post-Docs in Bold*)

Biederman, J, A Harpold, D Gochis, BE Ewers, **D Reed**, S Papuga, P Brooks. 2014. Compensatory vapor flux reduces water for streamflow following severe bark beetle-induced forest mortality. Water Resources Research 50(7):5395-5409.

Borkhuu, B, SD Peckham, U Norton, BE Ewers, E Pendall. Accepted with Major Revisions. Soil respiration declines following beetle-induced forest mortality in a lodgepole pine forest. Agriculture and Forest Meteorology.

Ewers, BE. 2013. Understanding stomatal conductance responses to long-term environmental changes: A Bayesian framework that combines patterns and processes. Tree Physiology. 33:119-122

Frank JM, WD Massman, BE Ewers, L Huckabee, J Negron. 2014. Ecosystem CO2/H2O fluxes are explained by hydraulically limited gas exchange during tree mortality from spruce beetles. Journal of Geophysical Research-Biogeosciences. 119:1195-1215

Frank, JM, WJ Massman, E Swiatek, HA Zimmerman, BE Ewers. Accepted with Major revisions. Lack of transducer/structure shadowing correction explains observed underestimates in vertical wind velocity from some non-orthogonal sonic anemometers. J Atm & Oceanic Tech.

Hyde K, **S Peckham**, T Homes, BE Ewers. 2015. Bark beetle-induced forest mortality in the North American Rocky Mountains. Mortality effects in Forests. Elsevier ed. R Sivanpillia. Accepted pending revisions.

Norton, N, *BE Ewers*, **B Borkhuu**, E Pendall. 2015. Soil and litter nitrogen and greenhouse gas fluxes during five years of bark beetle infestation in a lodgepole pine forest. Soil Science Society of America Journal 79(1):282-293.

Peckham, SD, BE Ewers, DS Mackay, E Pendall, **JM Frank**, WJ Massman. Are simple models better? Bayesian analysis of a carbon cycle model and its respiration components. In preparation for Global Change Biology.

Reed, D, BE Ewers, E Pendall. 2014. Impact of mountain pine beetle induced mortality on forest carbon and water fluxes. Environmental Research Letters. 9:105004. Doi:10.1088/1748-9326/9/10/105004

Schlaepfer, DR, BE Ewers, BN Shuman, DG Williams, **JM Frank**, WJ Massman, WK Lauenroth. 2014. Terrestrial water fluxes dominated by transpiration: Comment. Ecosphere. 5:art61. Doi: 10.1890/ES13-00391.1

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(Invited participant) BE Ewers Workshop on Plant Mortality, Jena Germany, Oct 2014.

Frank, JM, Massman WJ, Williams DG, Ewers BE, Kipnis E. Does sublimation decline after a spruce beetle outbreak? Agriculture and Forest Meterology Meetings, Portand OR, May, 2014.

(Invited) Ewers BE. Hydraulic Limitations Help Explain the Behavior of Plants: from clocks to mortality to ghosts. Department of Biology, University of Northern Colorado. January, 2014.

Massman, WJ, **Frank, JM**, Swiatek, E, Zimmerman, H, Ewers, BE. Which are more accurate, orthogonal or non-orthogonal sonic anemometers? American Geophysical Union Meeting, San Francisco, CA. Dec, 2013.

Bowling, DR, Ewers, BE, et al. Land-atmosphere carbon cycle research in the southern Rocky Mountains. American Geophysical Union Meeting, San Francisco, CA. Dec, 2013.

Kipnis, E, Chapple, WD, Traver, E, **Frank, JM,** Ewers, BE, Miller, SN, Williams, DG. Spatial variability of snow water isotopes in montane southeastern Wyoming. American Geophysical Union Meeting, San Francisco, CA. Dec, 2013.

Brooks PD, Harpold, AA, Biederman JA, Gochis DJ, Litvak, ME, Ewers, BE, Broxton, PD, **Reed, DE**. Non-linear feedbacks between forest mortality and climate change: implications for snow cover, water resources, and ecosystem recovery in western North America. American Geophysical Union Meeting, San Francisco, CA. Dec, 2013.

Ewers BE, et al. Bark beetle impacts on ecosystem processes are over quickly and muted spatially. American Geophysical Union Meeting, San Francisco, CA. Dec, 2013.

Mackay, DS, Ewers, BE, Peckham, SD, Savoy, P, Reed, DE, Frank, JM. Towards scaling interannual ecohydrological responses of conifer forests to bark beetle infestations from individuals to landscapes. American Geophysical Union Meeting, San Francisco, CA. Dec, 2013.

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Peckham, SD, Ewers, BE, Mackay, DS, Pendall, E, Frank, JM, Massman, WJ. Simulating stand-level water and carbon fluxes in beetle-attacked conifer forests in the Western US. American Geophysical Union Meeting, San Francisco, CA. Dec, 2013.

(Invited) Ewers BE. Quantifying how bark beetles impact forest hydrology. Presentation to American Association for the Advancement of Science External Advisory Committee to UW EPSCOR.

(Invited) Ewers BE. Causes and consequence of bark beetle-induce mortality on water, carbon, and nitrogen cycling. Ecological Society of America Annual Meeting. Minneapolis Minnesota. August, 2013.

Peckham, SD, BE Ewers, DS Mackay, E Pendall, HN Scott, JM Frank, MG Ryan and WJ Massman. Bayesian analysis of a carbon cycle model: Implications for parameter estimation, model selection, and simulation of beetle-caused forest mortality. Ecological Society of America Annual Meeting. Minneapolis Minnesota. August, 2013.

Mackay, DS, BE Ewers, **SD Peckham**, PR Savoy, **D Reed**, **JM Frank**, NG McDowell. Plant hydraulic controls over the susceptibility of trees to mortality following climate-enhance disturbances. Ecological Society of America Annual Meeting. Minneapolis Minnesota. August, 2013.

(Invited) Ewers BE. Impacts of bark beetle outbreaks from stands to watersheds. Public Lecture Sponsored by UW Ruckelhaus Institute. Laramie, WY May 2013.

(Invited) Ewers BE. Impacts of bark beetle outbreaks from stands to watersheds. Public Lecture Sponsored by UW Ruckelhaus Institute. Steamboat Springs, CO May 2013.

(Invited) Ewers BE. Impacts of bark beetle outbreaks from stands to watersheds. Public Lecture Sponsored by UW Ruckelhaus Institute. Saratoga, WY May 2013.

(Invited) Ewers BE. Hydraulic Limitations Help Explain the Behavior of Plants: from clocks to mortality to ghosts. Department of Biology, U. of New Mexico, February, 2013

(Invited) Ewers BE. Hydraulic Limitations Help Explain the Behavior of Plants: from clocks to mortality to ghosts. Department of Biology, Los Alamos National Labs, February, 2013

(Invited) Ewers BE. Impact of Fire and Insect Disturbance on Water Cycling in Ecosystems. Land Managers of the Laramie District of the Medicine Bow National Forest. February 2013

(Invited) Ewers BE. Surprising effects of bark beetle-induced mortality on snowpacks and water yield. Wyoming Weather Modification Technical Advisory Team Meeting, Cheyenne, WY January, 2013.

(Invited) Ewers BE. Impact of bark beetle outbreaks on forest water yield. Wyoming Association of Conservation Districts. Casper, WY, December, 2012.

P.D. Brooks; A.A. Harpold; J.A. Biederman; M.E. Litvak; P.D.Broxton; D. Gochis; N.P. Molotch; P.A. Troch; B.E. Ewers. Insects, firests, and climate change: implications for snow cover, water resources and ecosystem recovery in Western North America. American Geophysical Union Meeting, San Francisco, CA, Dec. 2012.

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Peckham, SD, BE Ewers, DS Mackay**, JM Frank**, WJ Massman, MG Ryan, H Scott, E Pendall. Modeling net ecosystem exchange of carbon dioxide in a beetle-attacked subalpine forest using a data-constrained ecosystem model. American Geophysical Union Meeting, San Francisco, CA, Dec. 2012.

Mackay, DS, BE Ewers, **DE Reed**, E Pendall, NG McDowell. Plant hydraulic controls over ecosystem responses to climate-enhanced disturbances. American Geophysical Union Meeting, San Francisco, CA, Dec. 2012.

(Invited) Ewers BE. Impact of bark beetle outbreaks on forest water yield. Wyoming Water Development Commission. Cheyenne, WY, November, 2012.

(Invited) Ewers BE. Impact of bark beetle outbreaks on forest water yield. Joint meeting of the Wyoming Water Development Commission and the Select Water Subcommittee of the Wyoming Legislature. Casper, WY, November, 2012.

(Invited) Ewers BE. Impact of bark beetle outbreaks on forest water yield. Wyoming Water Association Annual Meeting. Lander, WY, October, 2012.

Reed, DE, BE Ewers, E Pendall, RD Kelly, U Norton, **FN Whitehouse**. Mountain pine beetle epidemic changes ecosystem flux controls of lodgepole pine. Ecological Society of America Annual Meeting, Portland, OR, August 2012.

Brooks, PD, HR Barnard, J Biederman, B Borkhuu, SL Edburd, BE Ewers, D Gochis, E Gutmann, AA Harpold, JA Hicke, DJP Moore, E Pendall, **D Reed**, A Somor, PA Troch. Multi-scale observation of hydrologic partitioning following insect-induced tree mortality: Implications for ecosystem water and biogeochemical cycles. Ecological Society of America Annual Meeting, Portland, OR, August 2012.

Frank, JM, WJ Massman, BE Ewers. Linking bark beetle caused hydraulic failure to declining ecosystem fluxes in a high elevation Rock Mountain (Wyoming, USA) forest. Ecological Society of America Annual Meeting, Portland, OR, August 2012.

Ewers BE, DS Mackay, E Pendall, J**M Frank, DE Reed,** WJ Massman, **TL Aston**, **JL Angstmann, K Nathani, B** Mitra. Use of plant hydraulic theory to predict plant controls over mass and energy fluxes in response to changes in soils, elevation and mortality. Ecological Society of America Annual Meeting, Portland, OR, August 2012.

Barnard, HR, A Byers, A Harpold, BE Ewers, D Gochis, P Brooks. Examining the response of lodgepole transpiration to snow melt and summer rainfall in subalpine Colorado, USA. Ecological Society of America Annual Meeting, Portland, OR, August 2012.

Brown, NR, U Norton, E Pendall, BE Ewers, **B Borkhuu**. High levels of soil and litter nitrogen contents after bark beetle-induced lodgepole pine mortality. Ecological Society of America Annual Meeting, Portland, OR, August 2012.

Ewers BE et al. Use of plant hydraulic theory to predict plant controls over mass and energy fluxes in response to changes in species, soils and mortality. American Society of Plant Biology Annual Meeting, Austin, TX, July, 2012.

(Invited) Ewers BE. Simulation modeling of bark beetle effects on stand water budgets. Wyoming Weather Modification Technical Advisory Team Meeting. Saratoga, WY July 2012.

Leveraged Support to this Project.
NSF ESPSCOR. Water in the West. $20 million total grant, Ewers PI. A major justification for this grant was the lack of correlation between increased water in stands and streams after bark beetle mortality. The TREES model funded by this project will now be tested against other, less biologically sophisticated hydrology models. This grant establishes the Wyoming Center for Environmental Hydrology and Geophysics (WyCEHG).

NSF ETBC Hydrologic Science. ETBC: Collaborative Research: Quantifying the Effects of Large-Scale Vegetation Change on Coupled Water, Carbon, and Nutrient Cycles: Beetle Kill in Western Montane Forests. CoPI Elise Pendall. $219,261. This NSF funding provided partial funding for several of the data sets used to test TREES.

Ag Exp Station and McIntire Stennis. Quantifying the impact of a massive mountain pine beetle outbreak on carbon, water and nitrogen cycling and regeneration of southern Wyoming lodgepole pine forests. CoPIs Elise Pendall and Urszula Norton $60,000. This grant provided partial funding for several of the data sets used to test TREES.

Mapping annual surface area changes since 1984 of lakes and reservoirs in Wyoming that are not gauged using multi-temporal Landsat data

Basic Information

Title:	Mapping annual surface area changes since 1984 of lakes and reservoirs in Wyoming that are not gauged using multi-temporal Landsat data
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Start Date:	3/1/2013
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Focus Category:	Water Quantity, Models, Education
Descriptors:	
Principal Investigators:	Ramesh Sivanpillai

Publications

There are no publications.

Final Report

Mapping annual surface area changes since 1984 of lakes and reservoirs in Wyoming that are not gauged using multi-temporal Landsat data

Focus Category: *Water Quantity (WQN), Models (MOD), Education (EDU)*
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SUMMARY

Data about water stored in lakes and reservoirs are essential for their prudent management. However if these water bodies are not gauged, information about the amount of water entering and leaving the reservoir is unknown. Without this information it is difficult for planners and policy makers to devise appropriate management plans. This research project tested the utility of Landsat data (collected and distributed at no-cost by US Geological Survey) to map surface area changes of seven Wyoming lakes and reservoirs that are not gauged. First, challenges associated with identifying various types of water bodies (clear, shallow and turbid) in Landsat images were tested. Mapping medium-large size water bodies (Bull Lake and Keyhole) off of Landsat images was relatively easier in comparison to small water bodies that were shallow or contained turbid water. Second, analyst bias and its influence on surface area estimation was more pronounced on small and turbid water bodies. However differences between analysts were relatively smaller for larger water bodies. Obtaining cloud-free images for some reservoirs was challenging which resulted in data-gaps in the time series. Findings from this research lead us to conclude that a) it is possible to map different types of water bodies using Landsat data, and b) analysts had to be trained with several sample images before they could gain the confidence to map water bodies. Methods developed through this proposal can be used in conjunction with the newly launched Landsat 8 data for mapping future surface area changes in Wyoming water bodies.

Another highlight of this project was the nine undergraduate students who were trained in remotely sensed image processing and information extraction techniques. Three student interns presented their research in the Geospatial Conference of the West held in Laramie (September 2013) and another student intern presented his work in the Wyoming Undergraduate Research Day held in Laramie (April 2014).

Mapping annual surface area changes since 1984 of lakes and reservoirs in Wyoming that are not gauged using multi-temporal Landsat data

1. INTRODUCTION

Mapping water surface area or shorelines of large water bodies with Landsat and similar moderate resolution satellite data is not new (Elmore and Guinn 2010). Spectral properties of water are distinct from most other land cover features (bare ground, forest, built surface etc) which makes the task of distinguishing them in remotely sensed images relatively easy (Campbell 2006).

Remotely sensed data collected by Landsat Thematic Mapper satellite since 1984 comprise a long time series of earth observation data (http://landsat.usgs.gov) that can be used for monitoring changes in earth's natural resources. Studies have shown that spatial and spectral resolutions of Landsat data can be used for mapping water bodies because of the spectral reflectance properties of water. Chen and Rau (1998) mapped shoreline changes in tidal areas using a series of Landsat images, and Ouma and Tateishi (2006) mapped changes in shorelines of the five East African Rift Valley lakes with Landsat images. However presence of suspended solids (turbid waters) or floating vegetation (algae for example) alters water's spectral reflectance thus posing some difficulties while processing the images (Jensen 2000).

Given the dynamic nature of water bodies (intra- and inter-annual changes) and also the fact the techniques developed at one location might not work elsewhere, it is imperative that the utility of Landsat data have to be tested at different areas of interest. This will enable us to identify problems that are unique to each location. Gray and Sivanpillai (2010) tested the utility of multi-temporal (1985-2009) Landsat data for mapping surface area changes in Ocean Lake, Wyoming. They reported that shallow portions along the western and southeastern portions of this lake posed some challenges to accurately delineate the shoreline. However when the water level was higher (i.e., more area) it was not a problem to delineate the shoreline.

Next step is to geographically extend the study conducted by Gray and Sivanpillai (2010) to include more reservoirs and lakes especially those that have complex shorelines, turbid waters, or presence of vegetation. The overall goal of the research project funded by the University of Wyoming Water Research Program was to estimate changes in surface area values of some reservoirs in Wyoming, especially those that are not gauged.

2. OBJECTIVES

a. Assess the suitability of Landsat images for mapping water bodies in Wyoming. Given the differences in shape and related characteristics of these lakes and reservoirs, it is not possible to use the same classification technique for all of them (objective #2 in the proposal).
b. Map surface area changes of the lakes and reservoirs that are not gauged for recording the amount of inflow and outflow. Some of these water bodies had records in the past but do not have gauges now, while for some either inflow or outflow but not both are measured (objective #1 in the proposal).

c. Water bodies to be mapped in this proposal will include Bull, Fontenelle, Glendo, Keyhole, Lower Sunshine, Park, Viva Naughton, Wheatland Reservoir #2, and Woodruff Narrows (objective #3 in the proposal).

3. METHODOLOGY

We downloaded 104 cloud-free Landsat images from the USGS data archives (GloVis http://glovis.usgs.gov and EarthExplorer http://earthexplorer.usgs.gov). Acquisition dates of these images spanned from 1984 through 2011. Individual spectral bands (3 visible and 3 infrared) were stacked and pixel digital numbers (DNs) were converted to the Top of the Atmosphere reflectance values using the methodology described by Chander et al. (2009).

At the end of the above step, we found that there were not sufficient cloud-free images for some reservoirs identified in section 2.c. Therefore we replaced these reservoirs with others identified from the managers and stakeholders during the Wyoming Water Association Meeting (October 2012, Lander, WY). Updated list of reservoirs (**objective c**) analyzed in this study: Cameahwait, Ray Lake, Washakie, Viva Naughton, Pilot Buette, Bull Lake and Keyhole reservoirs.

From each Landsat image subsets corresponding to the spatial extent of each reservoir were extracted and stored as a separate file (Figure 3.1). This process minimizes the chances for potential spectral overlap between water stored in the reservoirs and outside.

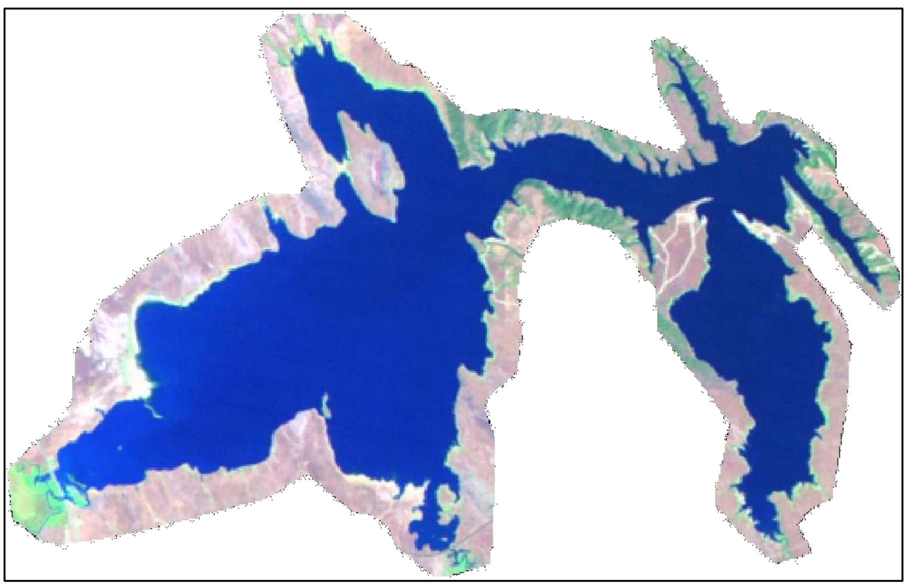


Figure 3.1. *Landsat 5 Thematic Mapper image clipped (or subset) to the spatial extent of Keyhole Reservoir. Clear and deep water appears in darker shades of blue, while shallow water appears in lighter shades of blue. Vegetation appears in green color.*

3.A. LANDSAT SUITABILITY STUDIES (PILOT PROJECTS)

As part of the first objective (**objective a**), Landsat data for the following reservoirs were used for pilot studies: Bull Lake, Cameahwait, Keyhole, Sand Mesa #1 and Sixty Seven.

Funding for this project was finalized only in June 2013. Hence resources from **WyomingView** (another USGS funded project through AmericaView) were used to recruit undergraduate interns to work on pilot projects. WyomingView student interns and the reservoir they selected for the pilot study are listed in table 1.

Table 1: Reservoirs mapped by the undergraduate student interns funded through the WyomingView internship program in spring 2013 semester

#	Student name & major	Reservoir	# of Landsat images
1	**Kate Richardson**, BS Rangeland Ecology and Watershed Management	Bull Lake	10
2	**Cody Booth**, BS Rangeland Ecology and Watershed Management	Cameahwait & Sand Mesa #1	5 & 5
3	**Bailey Terry**, BS Rangeland Ecology and Watershed Management	Key Hole	8
4	**Christopher Steinhoff**, BS Rangeland Ecology and Watershed Management	Sixty Seven	18

Water bodies included in these images represented a range of conditions: clear, turbid, and shallow. Few images had water bodies with floating vegetation. WyomingView interns classified each Landsat images in order to assess their suitability for mapping water bodies and documented the potential and limitations.

3.B. QUANTIFYING ANALYST BIAS

Analyst bias is part of any remotely sensed image analysis and can introduce errors in the estimated values of the surface area. To quantify the analyst bias, same sets of images were assigned to at least 3 analysts. Each analyst independently classified the images and mapped the surface area of the reservoir. File names of the images were scrambled and identities of analysts were kept confidential.

To quantify analyst bias, digitally classified Landsat data corresponding to 7 reservoirs (Table 2) were assigned to undergraduate interns and volunteers in fall 2013. Their task was to assign the clusters in the images to water or non-water thematic class. We provided classified Landsat images to each analyst instead of raw bands, in order to eliminate potential errors associated with classification procedures.

We also tested whether analyst's experience in image processing would result in differences in area estimates. So we requested 3 analysts with 1 year (undergraduate student), 10 years (volunteer) and 22 years (volunteer) of image processing experience to classify the same set of images.

Table 2: Reservoirs mapped by the undergraduate student interns funded through Water Research Program grant and volunteers.

#	Student name & major	Reservoir name	# of Landsat images
1a	**Shane Black**, BS Rangeland Ecology and Watershed Management	Anchor, Cameahwaitl, & Washakie (shallow reservoirs)	6 images each
1b	Julia Vold, BS Agricultural Business*		
1c	**Zac Tuthill**, BS Rangeland Ecology and Watershed Management		
2a	**James Scharffarzick**, BS Rangeland Ecology and Watershed Management	Gillette, La Prele, and Grey Rock (water with floating vegetation)	5 images each
2b	Thoa Pham, BS Agroecology*		
2c	**Mary Harris**, Undeclared major		
3a	**Bailey Terry**, BS Rangeland Ecology and Watershed Management	Keyhole Reservoir	6 images each
3b	Mike Pritchard, Undeclared Masters' student *		
3c	Ken Driese, Research Scientist, UW Botany*		

*volunteers

3.C. ESTIMATING SURFACE AREA CHANGES

Using the insights gained from steps 3.a and 3.b we classified Landsat 5 images acquired from 1986 through 2011 and extracted the surface areas of the reservoirs listed in objective 2.c. We used unsupervised classification techniques to extract the water surface areas from each image. We generated between 50 and 75 clusters during the classification which provided the flexibility to control the number of clusters that were assigned to water class. We did not try to distinguish different types of water bodies such as: clear, turbid or shallow.

4. PRINCIPAL FINDINGS

We accomplished all three objectives of this project. However we had to select a different reservoirs than the ones proposed because of the non-availability of cloud-free images. Findings from each objective are listed below.

4.A. LANDSAT SUITABILITY STUDIES (PILOT PROJECTS)

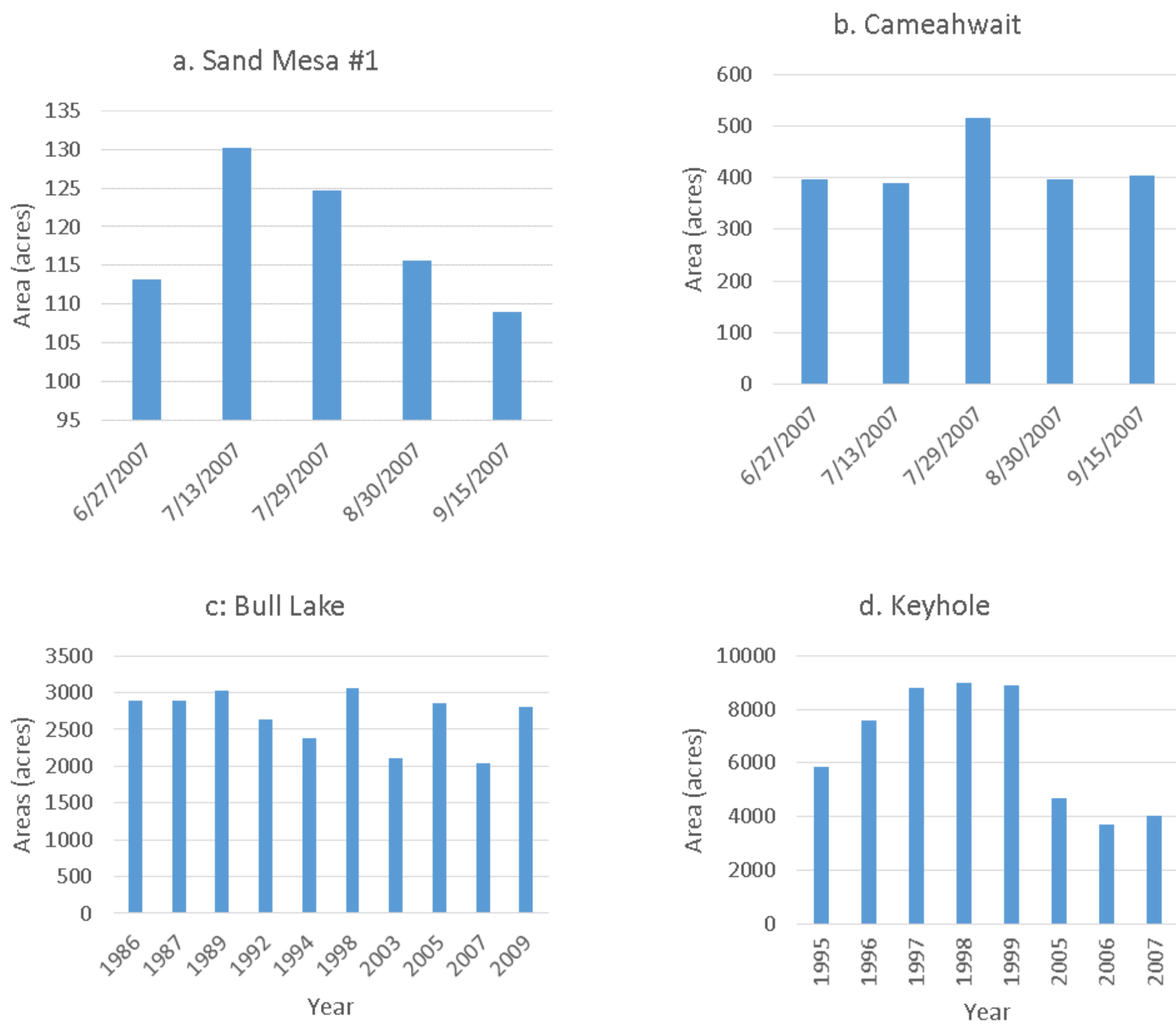


Figure 4.1: *WyomingView interns were able to successfully map the reservoirs off of the Landsat images. However consistently distinguishing shorelines both within and between the images posed challenges.*

Mapping large water bodies (Bull Lake and Keyhole) from Landsat images posed little to no problems (Figure 4.1). Spectral reflectance values of water bodies were distinctly different from surrounding features. Analysts were able to easily assign the clusters in the classified images to with relatively high degree of confidence. Delineating the shoreline posed some challenges to the analysts. However as they processed more images they become more confident with delineating the shorelines.

Mapping smaller water bodies that were shallow (Cameahwait) or contained turbid water (Sand Mesa #1 and Sixty Seven) was relatively more challenging to the analysts (Figure 4.1). As witnessed in the case of large reservoirs, as analysts processed more images they become more confident in delineating water bodies from Landsat images.

Results from these pilot studies lead us to conclude that a) we can map different types of water bodies using Landsat data, and b) analysts (students) had to be trained with several images before they could gain the confidence to map water bodies.

4.B. QUANTIFYING ANALYST BIAS

Classifying small lakes and reservoirs that were either shallow (Anchor Res.) or contained vegetation along the shoreline (Gillette Lake) from Landsat images posed major challenges. There were major differences in surface area estimates for these reservoirs which lead us to conclude that estimates derived for these and similar small lakes might not be consistent and also less accurate (Figure 4.2).

However as the surface area of the water bodies increased, differences in area estimates started to decrease. Analysts were also more confident in their results, which lead us to conclude that the effect of analyst bias will be minimum for medium to large size water bodies. Therefore estimates derived from different analysts will not vastly vary for such water bodies (Figure 4.2).

Shallow Reservoirs **Reservoirs with vegetation along the edges**

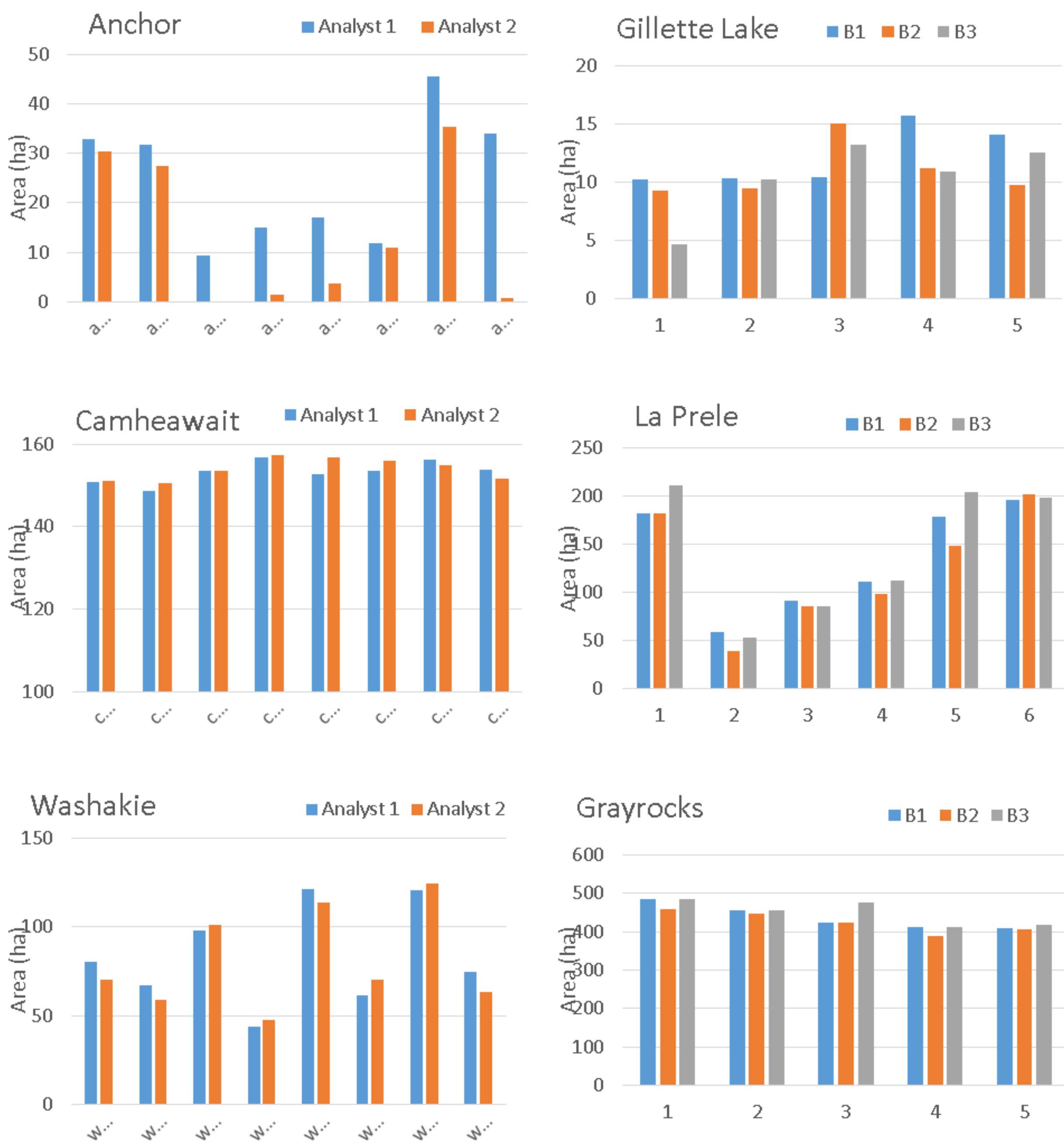


Figure 4.2: *Analyst bias in estimating water surface area of different reservoirs. Images of Anchor, Camheawait and Washakie reservoirs were mapped by two analysts (1 and 2), while Landsat images of Gillette, La Prele and Grayrocks reservoirs were mapped by three analysts (B1, B2 and B3). Area estimates of Anchor reservoir showed most differences between analysts.*

Analysts experience with image processing had a small influence in the area estimates they derived from each image. Analysts with 10+ years of experience combined some of the edge pixels with the main water body, however the analyst with least experience did not do so (Figure 4.3). This outcome might have to do with their level of familiarity with hydrological issues.

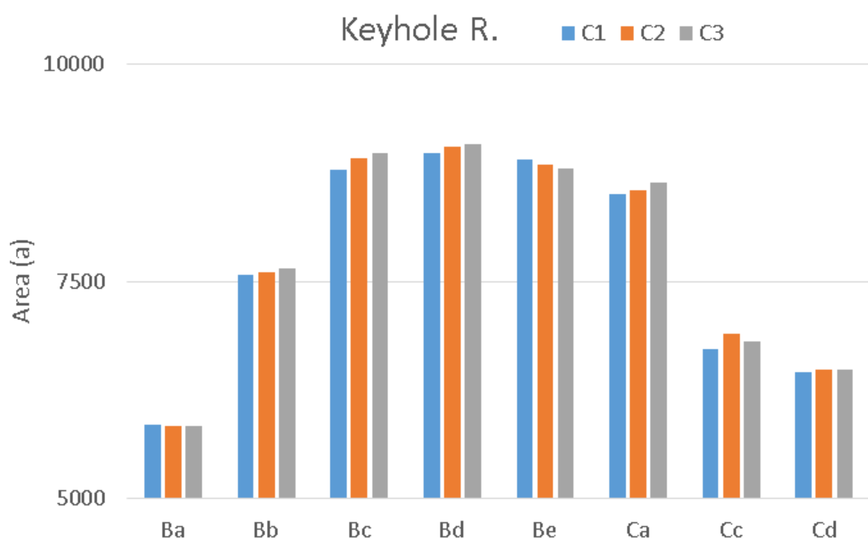


Figure 4.3: *Water surface area estimates derived from eight Landsat images by three analysts (C1, C2 and C3) who had one, ten and twenty plus years of image processing experience respectively.*

4.C. SURFACE AREA CHANGES

Based on the insights gained from the pilot studies we developed a set of image classification protocols for delineating water bodies from Landsat images and estimating their surface areas. Images were clipped close to the boundary of the reservoirs in order to minimize spectral confusion from Earth surface features outside the reservoir. Second, we decided to exclude the pixels representing shorelines and classified only those pixels that contained some water which was determined by their appearance in Landsat band combinations 4, 3 and 2. Finally analysts were required to classify several images in order to familiarize them to the unique characteristics of the landscape surrounding the reservoirs.

Surface area estimates of the reservoirs derived from Landsat images are displayed in Figures 4.4 – 4.10. For some reservoirs it was difficult to obtain cloud-free images in August, so we included images from September and in rare instances from July as well. However for some reservoirs (Bull Lake for example) it was difficult to obtain any cloud-free image from July through October. This resulted in data gaps in the time-series. Since there will be differences between seasons we did not use images from spring or summer to fill these data gap.

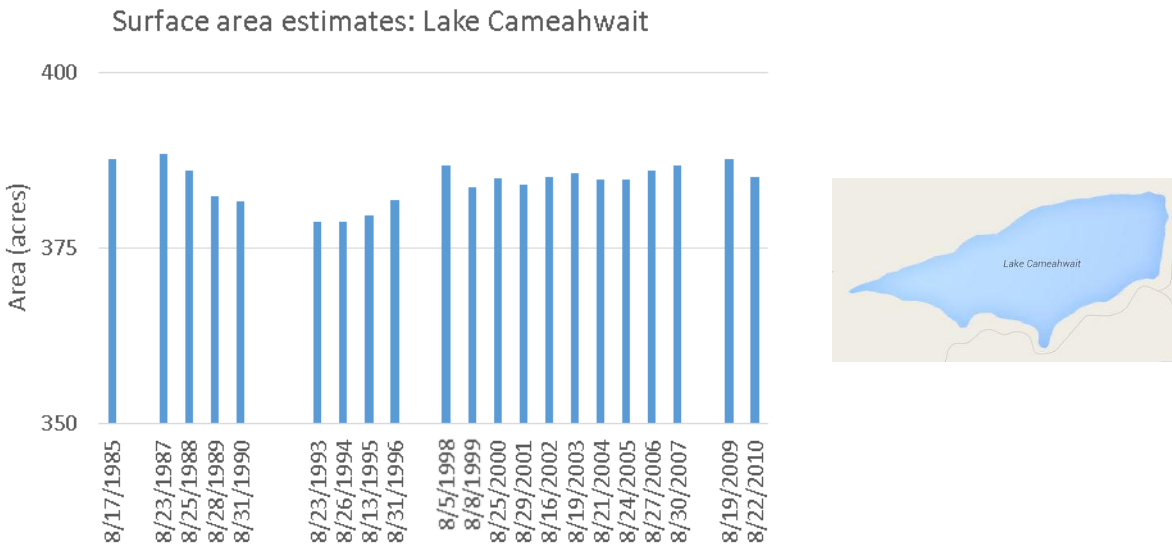


Figure 4.4: *Surface area estimates for Lake Cameahwait derived from Landsat 5 TM images acquired from 1985 through 2011 in the month of August.*

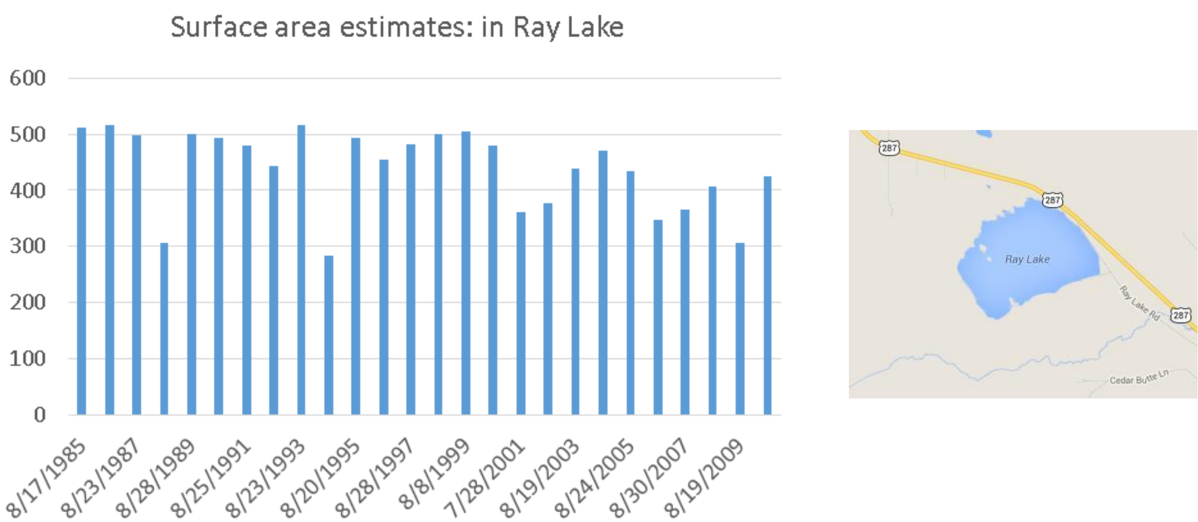


Figure 4.5: *Surface area estimates for Ray Lake derived from Landsat 5 TM images acquired from 1985 through 2011 in the month of August.*

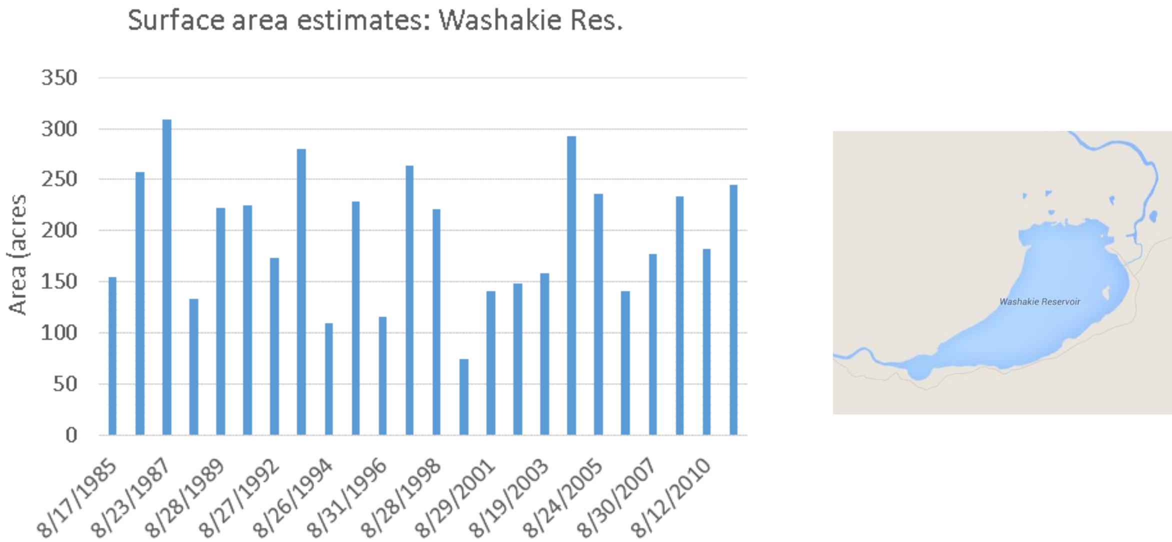


Figure 4.6: *Surface area estimates for Washakie Reservoir derived from Landsat 5 TM images acquired from 1985 through 2011 in the month of August.*

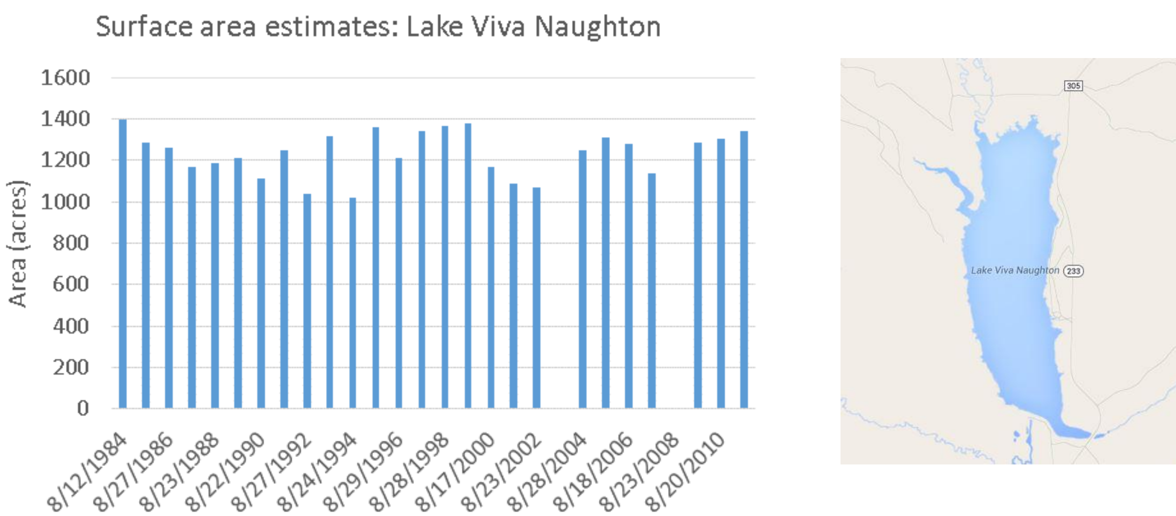


Figure 4.7: *Surface area estimates for Lake Viva Naughton derived from Landsat 5 TM images acquired from 1985 through 2011 in the month of August.*

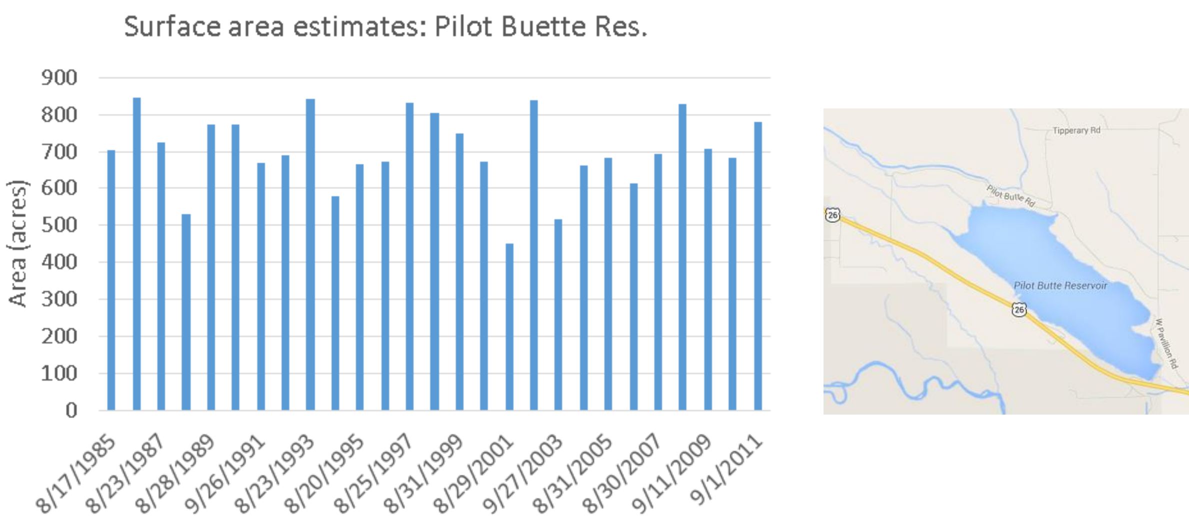


Figure 4.8: *Surface area estimates for Pilot Buette Reservoir derived from Landsat 5 TM images acquired from 1985 through 2011 mostly in the month of August. Four images were acquired in September, and one image was acquired in July.*

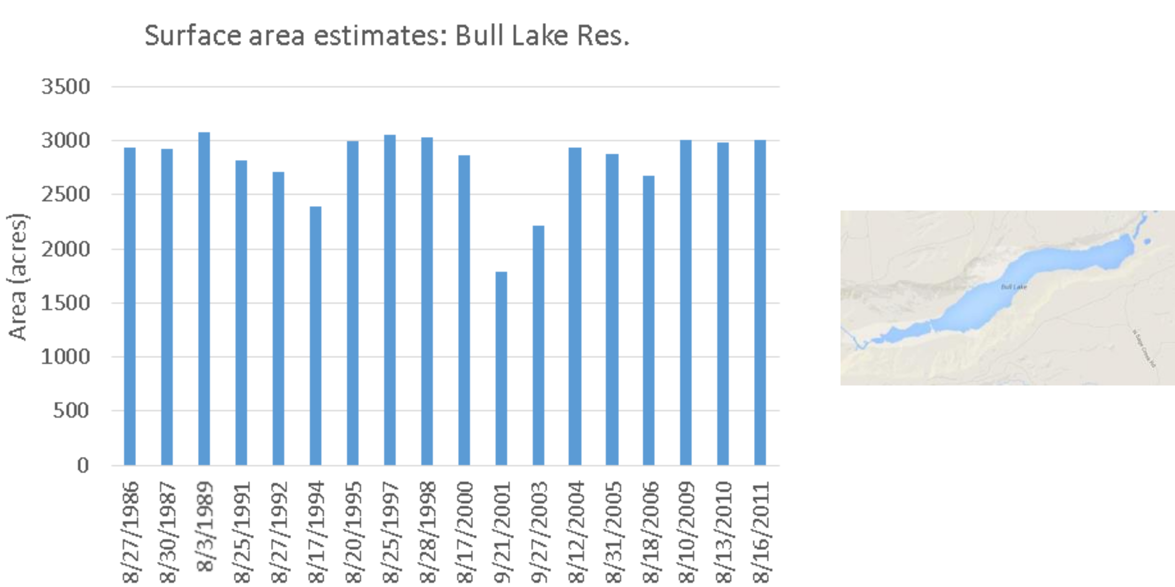


Figure 4.9: *Surface area estimates for Bull Lake Reservoir derived from Landsat 5 TM images acquired from 1986 through 2011 mostly in the month of August.*

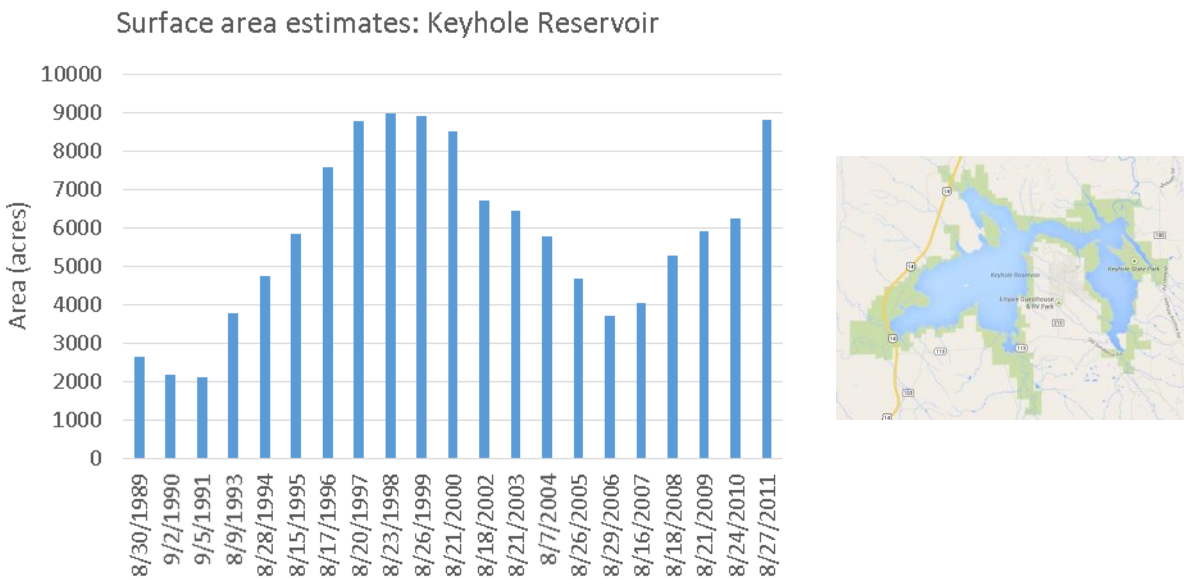


Figure 4.10: *Surface area estimates for Keyhole Reservoir derived from Landsat 5 TM images acquired from 1989 through 2011 mostly in the month of August.*

5. SIGNIFICANCE

This research project tested the utility of mapping surface area changes since 1984 in several small to medium sized reservoirs in Wyoming. Results obtained from this research suggest that Landsat data collected and distributed by the USGS can be used for estimating past surface area values of reservoirs in Wyoming. This information will be useful for those reservoirs that are gaged. Managers and policy makers can use this information to gain insights about how lake surface areas have changed since mid-1980s.

This study focused on creating a time-series consisting of late-summer, early-fall images. Since Landsat data were collected once in every 16 days it is possible to estimate surface area changes at that interval provided there are no clouds above the reservoir. Landsat data are provided at no-cost to users by the USGS.

Remotely sensed data used in this study was collected by Landsat 5 Thematic Mapper sensor which operated from 1984 through 2011. Landsat 7 (launched in 1999) continues to collect data however only 20% of each image is useful. The newest satellite in this series, Landsat 8 was launched in Feb 2013 and data are available from May 2013. Newly included spectral bands of Landsat 8 will improve the ability to water bodies.

Satellite derived surface areas of the reservoirs studied in this project and Ocean Lake (Gray and Sivanpillai 2010) will provide value valuable insights for mapping other reservoirs in Wyoming.

6. STUDENTS SUPPORTED & THEIR TESTIMONIALS

Total number of students supported in fall 2013: **8**

Total number of students supported in spring 2014: **1**

6.A. FALL 2013

Shane Black
BS, Rangeland Ecology and Watershed Management
Class: RNEW 4130 Applied Remote Sensing

I think that there is a bright future for studying water using remote sensing. I could see a lot of people using remote sensing and the correct software in the future for water identification. I do believe that there are limitations with measuring water using just unsupervised classification but with a combination of field work and unsupervised classification this can be a useful tool. I enjoyed taking part in this study it really helped me master some aspects of remote sensing.

Ryan Lermon
BS, Rangeland Ecology and Watershed Management
Class: RNEW 4130 Applied Remote Sensing

I found this water project to be very interesting, and it made me want to learn more about remote sensing. It is exciting that even though using satellite imagery for remote sensing has be around since the 1970's there is still much to learn. There are processes that still need to be refined or improved forty years later. It was somewhat difficult to find much research along the same lines that I was doing. To me this says that there is room for further study and improvement in this area of remote sensing.

Jimmy Schaffarzick
BS, Rangeland Ecology and Watershed Management
Class: RNEW 4130 Applied Remote Sensing

Throughout this experience, I have gained knowledge about both remote sensing and technological advancements that I never thought were possible. I have learned how to remotely sense water bodies, along with the challenges that arise with the process. I have learned how to use remotely sensed data to make management decisions in my future career. This project has greatly benefitted me, and I will use these many lessons for the rest of my life.

Zachariah Tuthill
BS, Rangeland Ecology and Watershed Management
Class: RNEW 4130 Applied Remote Sensing

This project broadened my knowledge of remote sensing and it applications. It also illustrated the impact of human bias and error, even in highly technological sciences like remote sensing. The need for accurate and reliable data about water is high, especially here in the west. Knowledge of how this data is collected and analyzed can only help me as I move forward toward a career in resource management.

Mary Harris
Undeclared graduate student
Class: BOT 4130 Applied Remote Sensing

My class project for BOT4130 was part of a larger study for the Wyoming Water Research Program. During this project I learned how to map reservoirs from Landsat5 satellite images, and I developed my own technique for assigning groups of pixels to specific landscape categories. Having my work be part of a larger study encouraged me to conduct my research on a professional level.

Elissa Paranto
BS, Biology Program
Class: BOT 4130 Applied Remote Sensing

I learned so much from this project, I do not know where to begin. This class was something I had no experience with in the past and was a challenge for me that I gladly accepted. This project took everything we learned all semester and applied it all into one huge lump sum. I have learned how to navigate excel and ERDAS with proficiency. I have also learned that mapping water's edge is a difficult feat to be had. Distinguishing water from the edge is a valuable measure of research to study for accurate readings of water levels for things like drought control and marine life. It is much more manageable then venturing out and doing ground work. I learned an immense amount and look forward to applying it in my future endeavors.

Ian Walker
BA Secondary Education/Social Studies
Class: BOT 4130 Applied Remote Sensing

I enjoyed working on this project because water management will be a consistent issue in the Western United States as future drought conditions are predicated. With so many lakes and reservoirs not regularly checked, water management is insufficient for this area. I learned that with the use of remote sensing and other techniques, it is possible to measure the amount of water, at a given location, and even be able to predict the water capacity during wet or dry years.

Erik Collier
B.S. Rangeland Ecology & Watershed Management
Class: BOT 4965 Undergraduate Research Remote Sensing

I previously completed an internship in remote sensing but with burn severity instead of mapping water. By mapping water I have gained another valuable skill to benefit my career. I will be working for the Bureau of Land Management and I feel mapping water can be useful in monitoring our allotments, by knowing how different areas are affected by drought. I am fortunate to have gained this skill set and can only see it benefiting my professional career. I would like to thank the Wyoming Water Research Program for the scholarship opportunity.

B. SPRING 2014

Zachariah Tuthill
BS, Rangeland Ecology and Watershed Management
Class: RNEW 4990 Digital Image Processing for Natural Resource Management

This Water Research Program internship helped me gain a deeper understanding of the utility and application of remote sensing in natural resource management. As management concerns grow especially as they pertain to water in the west, the knowledge to use and apply this kind of information is sure to be a benefit to me. Presenting my research at the Undergraduate Research Day helped develop my communication skills and my confidence.

7. PRESENTATIONS *(STUDENTS ARE ITALICIZED)*

Total number of conferences/events: **2**

Total number of students: **4**

Tuthill, Z, Sivanpillai, R. 2014. Mapping water bodies with Landsat imagery contaminated with thin layer-clouds. 2014 Wyoming Undergraduate Research Day, Laramie, WY. April 26.

McCollum, K, Thoman, MJ. 2013. Transferability of Landsat-derived NDWI Values across space and time. Geospatial Conference of the West 2013, Laramie, WY. Sept 16-19.

Terry, B. 2013. Characterizing analyst bias in unsupervised classification of Landsat images. Geospatial Conference of the West 2013, Laramie, WY. Sept 16-19.

8. CITATIONS

Campbell JC (2006) Introduction to Remote Sensing. The Guilford Press, NY
Chander (2009) Remote Sensing of Environment 113:893–903
Chen L, Rau J (1998) Remote Sensing of Environment - 19:3383-3397
Elmore A, Guinn S (2010) Remote Sensing of Environment - 114:2384-2391
Gray WL, Sivanpillai R (2010) GIS in the Rockies – 2010 presentation. Loveland, CO
Jensen J (2000) Introductory Digital Image Processing: A Remote Sensing Perspective. Prentice-Hall, Englewood Cliffs, NJ

Micro-Patterned Membrane Surfaces with Switchable Hydrophobicity

Basic Information

Title:	Micro-Patterned Membrane Surfaces with Switchable Hydrophobicity
Project Number:	2013WY85B
Start Date:	3/1/2013
End Date:	2/28/2015
Funding Source:	104B
Congressional District:	1
Research Category:	Water Quality
Focus Category:	Treatment, Wastewater, Water Supply
Descriptors:	None
Principal Investigators:	Carl Frick, Jonathan Brant

Publication

1. Laursen, C. M., 2014. “Proof-of-concept switchable hydrophobic/hydrophilic patterned surfaces from thermo-mechanically tailored acrylate systems,” M.S. thesis, Dept. Mech. Eng., Univ. of Wyo., Laramie, WY, December, 64 pgs.

Final Report

Micro-Patterned Membrane Surfaces with Switchable Hydrophobicity

PIs: Carl Frick, Department of Mechanical Engineering, University of Wyoming
Jonathan Brant, Department of Civil Engineering, University of Wyoming

Dates: March 1, 2013 – February 28, 2015

Abstract:

Interest in, and the use of, membrane distillation for desalination applications is growing in areas like Wyoming that are grappling with dwindling freshwater supplies and the large volumes of saline water that are generated from the development of our energy resources. Realizing the full potential of membrane distillation hinges on the development of new membrane materials that are tailored for the unique requirements of this process. The *overarching goal* of this research was the synthesis, characterization, and testing of a preliminary hierarchical membrane surface coating whose properties can be changed in response to environmental stimuli. The *objective* was to create a structured surface capable of switchable hydrophobicity. It was our *central premise* that a biologically inspired patterned surface manufactured through conventional soft molding techniques using shape-memory polymers, will create a highly hydrophobic surface when erect, while demonstrating dramatically less hydrophobicity when in a relaxed state, as a result of the relationship between surface roughness and hydrophobicity. Such a surface would facilitate easier cleaning of the membrane by backwashing, while maximizing the separation efficiency and permeate flux rate through the membrane. Our *rationale* for undertaking this research was that new treatment strategies, like membrane distillation, are needed to effectively manage highly saline waters. We accomplished the overall objective of this proposal by pursuing the following specific aims:

Specific Aim #1 – Synthesize membrane surface treatments from shape-memory polymers having tunable surface structure controlled hydrophobicity. Standard soft molding techniques were used to fabricate proof of concept, small-scale pattern, consisting of arrays of vertical micro-pillars. These pillars were supplemented with spatially tailored surface treatments to further enhance the overall switchable wettability effect.

Specific Aim #2 – Assess and evaluate the efficacy of membrane surfaces with tunable surface structure and hydrophobicity. We characterized the structure and hydrophobicity of the shape-memory polymer structures as a function of environmental parameters relevant to membrane distillation applications and evaluated any changes in polymer structure in terms of their impact on membrane performance.

1 Purpose and Objectives:

The overarching goal of this research was to create a proof-of-concept structured surface that could ultimately be cast onto water filtration membranes out of a unique, multi-tiered platform consisting of a thermo-mechanically tailored polymer understructure arrayed in a pillared pattern that is overlaid with various hydrophobic/hydrophilic surface treatments. It is through the combination of the underlying polymer system, preferential surface treatments, and patterned structure that the effect is believed to assist in the anti-fouling properties and aid in "self-cleaning" during membrane backwashing.

It is our central premise that a biologically inspired micro-patterned surface manufactured through conventional molding techniques using thermo-mechanically tailored acrylate based polymers as well as various surface treatments will assist in antifouling in two ways. First, through a change in wetting characteristics. It is our hypothesis that we could create a highly hydrophobic surface when erect, while demonstrating a dramatically less hydrophobic - even hydrophilic - system when in a relaxed state, as a result of the relationship between surface roughness and surface chemistry. Through this stark change in characteristics, it is possible to deter a wide array of fouling materials based off their specific surface interactions, whether hydrophilic or hydrophobic in nature instead of targeting just one specific group. At the same time, the geometrical structuring of the pillars are expected to continue to allow for water transport across the membrane even in a hydrophobic state because of the expected size scale, allowing for advective transport to the membrane similar to that seen in porous membranes [1].

Second, is through the mechanical alteration of the material properties within the structured surface. Through changing the material from a rigid state to a pliable state with an increase in temperature, it was hypothesized that a buildup of fouling materials will be destabilized and encouraged to break off during the back flushing process, continuing into the waste stream, lowering the amount of irreversible fouling inherent to the pressure driven membrane process. This proposed process can be seen in **Figure 1**.

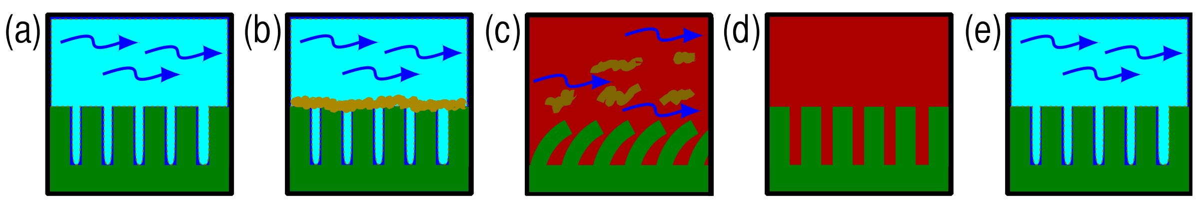


Figure 1: Proposed cleaning process and switching between hydrophobic to hydrophilic states on a micro-patterned surface. (a) The structured surface in normal operating conditions. (b) Significant fouling has built up. (c) The pillars become pliable under heating while crossflow continues, encouraging breakoff. (d) Halting of crossflow, and recovery of original shape. (e) Normal operation conditions commence.

In **Figure 1** (a), the structured surface appears in normal operating conditions at low temperatures and hydrophobic state. After significant fouling has built up in (b), the water is heated while the crossflow continues, and the pillars become pliable, switching to a hydrophilic state; encouraging breakoff (c). At the end of the cleaning process crossflow pressure is stopped, allowing the pillars to return to an undeformed state (d). The material is then cooled to a lower temperature for normal operations to resume in (e).

The research preformed here lays out the foundation for which future research can build upon, while steps in the future can focus on decreasing the overall size scale, optimizing pattern parameters, and manufacturing techniques to place this on an operating membrane. Our rationale for undertaking this research is that new treatment strategies, like membrane distillation, are needed to effectively manage highly saline waters. The ultimate goal of the Investigators is to leverage these results towards an SBIR proposal geared toward developing our switchable hydrophobic surfaces for commercial applications.

2 Problem:

Population growth, energy development, and agricultural interests are all competing for the limited freshwater supplies in Rocky Mountain region. As such, both industry and the public sector are using less pristine raw water sources such as brackish groundwater and oil and gas produced waters in an attempt to develop new water supplies [2]. Desalination is therefore receiving serious interest across the western US, for managing produced waters and augmentation of drinking water supplies [3,4]. Membrane fouling owing to high-energy requirements on the part of pressure driven membrane processes however remain significant challenges to processes like reverse osmosis (RO). An important need is the development of a membrane surface coating whose surface structure may be manipulated, i.e., a smart surface, to be rigid during process operation and flexible to facilitate backwashing the membrane during cleaning to optimize permeability recovery. The development of new materials whose surface properties may be controlled so as to provide greater flexibility in process operation is needed to realize the full potential of membrane distillation processes. In the absence of such advancements, the use of membrane distillation in desalination applications will be stagnated, particularly for produced waters, which have high total dissolved solids (salt) concentrations.

3 Methodology:

The research approach for this project could be broken into five major steps. Steps included (1) investigation into fundamental thermo-mechanical observations of nine acryl-based macromolecules (five monofunctional and four multifunctional) chosen from the broad class of acrylate monomers. The nine macromolecules were initially selected based off their expected low toxicity, ability to be polymerized through a chain polymerization process activated by a photointiator, and based off a diverse variety of functional groups allowing for a range of wetting characteristics and glass transitions. These select compounds can be seen in **Figure 2**.

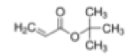
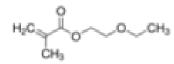
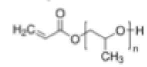
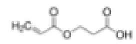
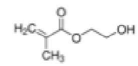
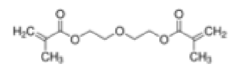
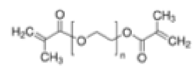
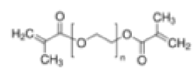
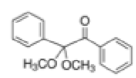
	Material	Structure	Molecular Weight (g/mol)
(a)	tert-Butyl acrylate (tBA)		128.17
(b)	2-Ethoxyethyl methacrylate (2EEM)		158.19
(c)	Poly(propylene glycol) acrylate (PPGA)		~475
(d)	2-Carboxyethyl acrylate (2CEA)		144.13
(e)	2-Hydroxyethyl methacrylate (2HEMA)		130.14
(f)	Di(ethylene glycol) dimethacrylate (DEGDMA)		242.27
(g)	Poly(ethylene glycol) dimethacrylate M_n 550 (PEGDMA550)		~550
(h)	Poly(ethylene glycol) dimethacrylate M_n 750 (PEGDMA750)		~750
(i)	Dipentaerythritol penta-/hexa-acrylate (DPPHA)		524.51
(j)	2,2-Dimethoxy-2-phenyl -acetophenone (DMPA)		256.3

Figure 2: Name, structure, and molecular weight of (a-e) monofunctional acrylates, (f-i) multifunctional acrylates, and (j) photoinitiator

Careful analysis of these materials fundamental thermo-mechanical behavior and water absorption characteristics provided insight into the best monomers to be blended for the specific application. Requirements of the final polymer system include stiffness changes within a distinct, narrow temperature window, limited water absorption characteristics, overall non-toxicity, the ability to be photopolymerized, and acceptable mechanical properties in the low and high temperature states.

With this underlying knowledge step (2) included a systematic alteration of relative weight percent of a ternary polymer network consisting of three of the select macromolecules, tert-Butyl acrylate, 2-Hydroxyethyl methacrylate, and Poly(ethylene glycol) dimethacrylate Mn550 to reach optimal thermo-mechanical properties in submerged and unsubmerged conditions. Once the polymeric network was custom tailored to display appropriate water absorption characteristics and adequate material stiffness changes within the select temperature range, step (3) characterized additional mechanical properties of the custom tailored system at various temperatures, ensuring a robust system.

Step (4) established molding techniques creating structured, patterned surfaces at a laboratory scale through investigation of two processes including a direct molding process and a soft molding process. The final step, (5), investigated various surface treatments that could be applied to the previously designed polymer, allowing for either a hydrophilic or hydrophobic surface. Again, as with the base polymer network, any treatments needed to be expected to have low toxicity, and be robust. In addition, they needed to leave the characteristics of the polymer substrate intact; as altering the mechanical behavior, water absorption, or temperature transitions that were customized for the specific application in steps (1-3) would be counterproductive. The final requirement of surface treatments is the ability to preferentially layer the system to enhance the structured surfaces hydrophobic and hydrophilic effects.

Investigation was made through a series of systematic studies incorporating polymer synthesis, various thermo-mechanical tests utilizing Dynamic Mechanical Analysis (DMA) and temperature dependent load frame testing, observation of water absorption characteristics, molding techniques, and various surface characterization techniques.

6 Principal Findings:

6.1 Base Polymer Networks

Initially, nine acryl based macromolecule systems were investigated both for their thermo-mechanical behavior as well as water absorption in order to ultimately isolate an optimal combination of systems based on aqueous glass transition behavior, water absorption, and mechanical properties. For the proposed application it was determined that the polymer systems must exhibit good shape-memory properties targeted for an onset temperature of approximately 30-40°C under submerged conditions, appropriate high and low temperature mechanical properties including strain-to-failure, and the ability to be photopolymerized into a structured surface. Five of these initial systems were monofunctional (linear-builders), while the remaining four were multifunctional (crosslinking) molecules. To ensure good shape-memory effects, both linear builders, as well as a light amount of crosslinking are necessary. A small amount of crosslinking in the system is added for two reasons: it will allow for hard segments needed for the polymer to remember its initial shape, and to assist in a well-established rubbery regime. However, too much crosslinking and the material ductility will greatly decrease. Additionally, the amount of cross linking is expected to dramatically affect the amount of water absorption due to an alteration in the amount of free volume in the polymer network. The nine macromolecules were chosen from a broad family based on ease of fabrication and nontoxicity.

Water absorption testes were run using ultra-pure water over a duration of 10 days; results can be seen in **Figure 3**. For linear builders, water absorption ranged from 53.8 ± 1.2% to 0.94 ± 0.47% represented by 2HEMA and tBA. Water absorption for pure crosslinkers ranged from 44.2 ± 2.7% to 3.9 ± 1.2% as PEGDMA750 and DEGDMA. The water absorption reached steady state for all synthesized polymers within approximately one day. It is worthy of note that 2CEA is not included in the part (a) of the figure as it dissolved in the water within the initial testing period of 1 hour.

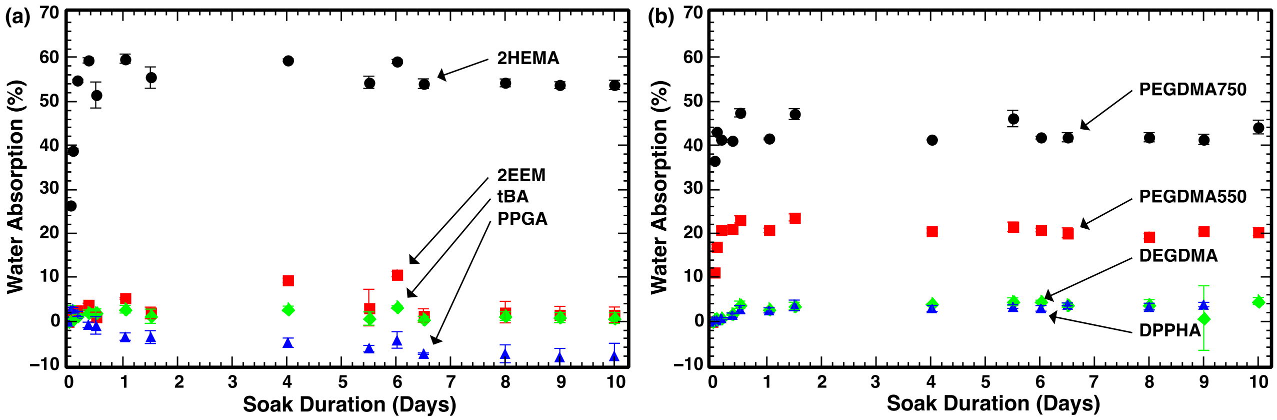


Figure 3: Water absorption for individual (a) monofunctional and (b) multifunctional acryl systems. Note 2CEA dissolved in water and therefore has not been included.

Initial thermo-mechanical testing of soaked samples was performed using the DMA to observe each constituents dry glass transition temperature, storage modulus in the rubbery and glassy regime, and shape-memory properties reflected in **Figure 4**. A material is expected to exhibit promising shape-memory effects if there is a large transition in the storage modulus over the transition region, altering the material from a stiff, rigid state to a soft, pliable state as temperature, combine this over a short temperature range and the result is a steep transition region such as the tBA curve of **Figure 4**.

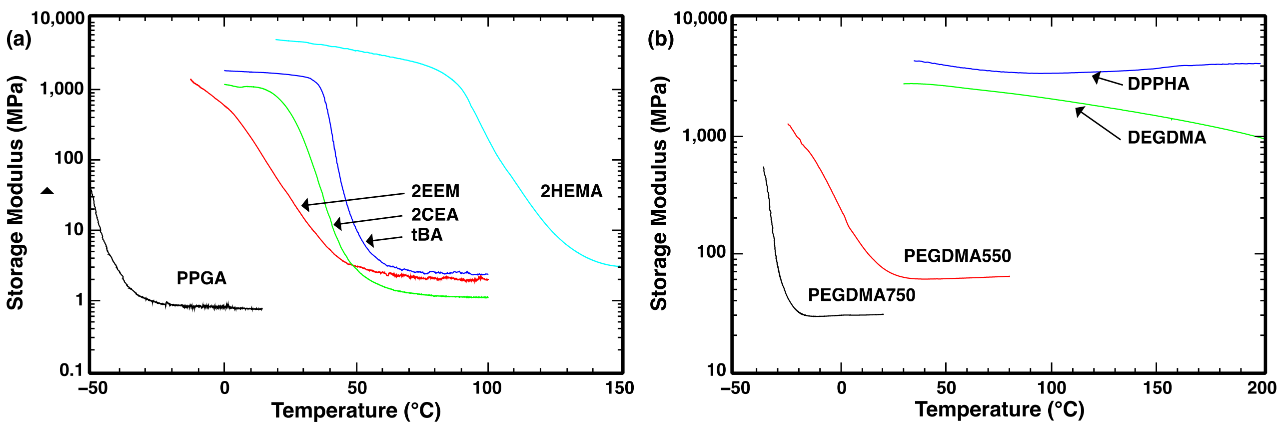


Figure 4: Representative curves of storage modulus transition as a function of temperature for individual (a) monofunctional and (b) multifunctional acryl systems. Results obtained from DMA.

6.2 Ternary Polymer Networks

Based on the observations in the last section, three polymer constituents were chosen to systematically vary including the linear builders tBA and 2HEMA, along with a small weight percentage of the crosslinker PEGDMA550. The choices of macromolecules were based on water absorption properties and promise of good shape-memory characteristics at the desired onset temperature around 30-45°C when soaked. As aforementioned, a light amount of crosslinking has historically shown better shape-memory effects. Because of this, the weight percentage of PEGDMA500, the crosslinker and DMAPA, the photoinitiator were held constant at 5% and 0.5% of the total respectively, while the relative percentage of tBA to 2HEMA were varied in six sample sets. Note that 2HEMA has a high water absorption at 53.8

± 1.2%, while tBA was much lower 0.94 ± 0.47% in **Figure 3**. Therefore through the varying the relative percentage, an alteration in the amount of water absorption is expected. This is reflected in **Figure 5**. In the figure the relative percentage of the 94.5% linear building solution change from 100/0, 90/10, 75/25, 50/50, 25/75, 0/100, tBA to 2HEMA.

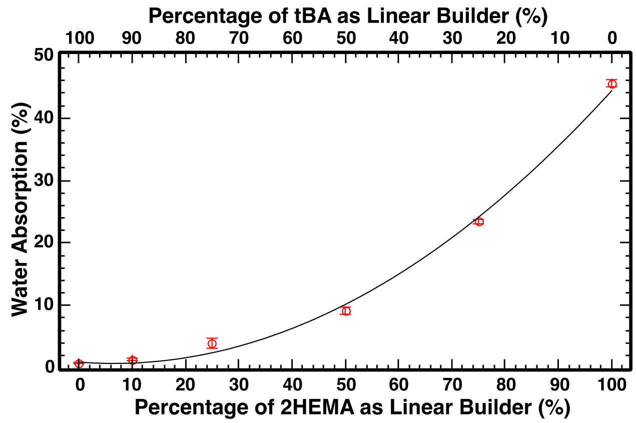


Figure 5: Water absorption as a function of varying the relative amounts of tBA and 2HEMA in a system with 5 wt.% PEGDMA550.

As the percentage of 2HEMA in the system increased there was an increase in the water content displayed in the curve fit. The target water absorption of approximately 4% of the materials original mass was a predetermined value.

Figure 6 (a) displays representative curves of storage moduli with samples in dry form. The glass moduli of the materials are relatively consistent ranging between 2 and 3 GPa, while the rubbery modulus of the materials range from approximately 1 to 10 MPa. General trends observed as the monofunctional builder mixture transitioned from a low percentage of 2HEMA to a low percentage of tBA is an increase in the glass transition temperature, and a gradual lengthening of the transition region.

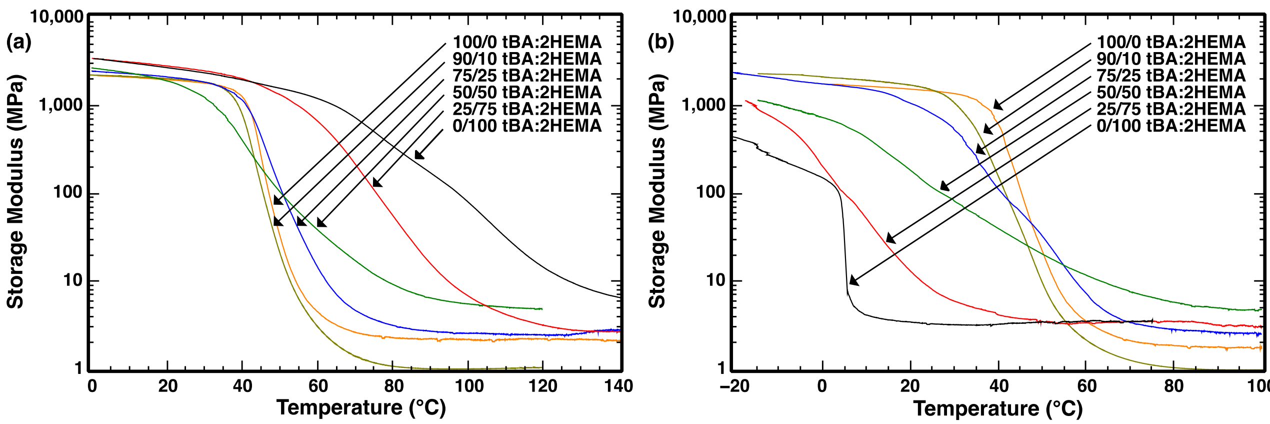


Figure 6: Representative (a) dry and (b) soaked DMA tests maintaining 5 wt.% PEGDMA550, while varying the relative wt. ratio of linear builders tBA and 2HEMA.

Similarly **Figure 6 (b)** shows the results of DMA testing for soaked samples. However, as the amount of 2HEMA increases in the linear building mixture now, the glass transition of the material tends to decrease. This is indicative to the amount of water absorbed into the system, as compared to **Figure 5** seen before.

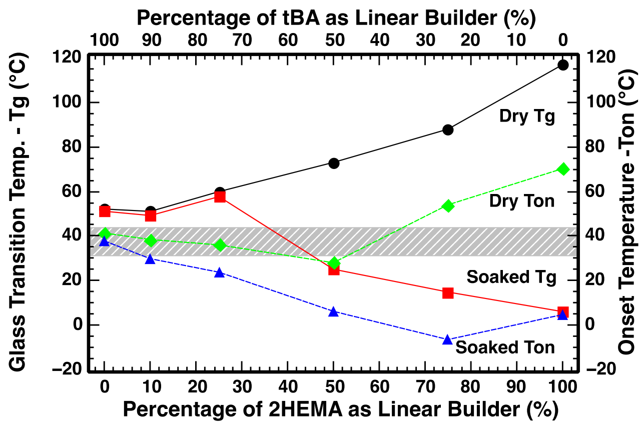


Figure 7: Effect on glass transition temperature and onset temperature as a function of varying the relative amounts of tBA and 2HEMA in a system with 5 wt.% PEGDMA550 for both dry and soaked samples.

To clarify results, a trend of both the glass transition temperatures and the onset temperatures of soaked and dry samples are displayed in **Figure 7**. The glass transition temperature is defined here as the peak of the Tan Delta curve, which has been omitted for clarity, and the onset temperature chosen as the intersect of two tangent lines to the glassy and transition regions. Note the target region for the onset of the shape-memory transition is displayed as the hashed gray region between 30°C and 45°C. The effect of the water absorption into the polymer system can readily be seen in the figure as the glass transition greatly decreases. From this figure one can also infer the relative duration of the transition region. The difference between the T_g and T_{on} of the 100% tBA over the 50/50% tBA-2HEMA is an indication of a steep transition region vs. a more gradual transition, and can be compared to **Figure 6**. A steep transition is favored.

6.3 Mechanical Properties of Final Network

Once the ternary network was customized for (1) glass transition temperature and (2) water absorption, a detailed inquiry was further made into the DMA and mechanical properties of the material.

A representative result from DMA testing of the final network can be seen below in **Figure 8 (a)**. Storage modulus is plotted on the left-hand axis, while the materials Tan delta is plotted on the right, both as a function of temperature. A five order of magnitude change in the materials storage modulus over the temperature range can be seen and is indicative of a transition of the material from its glassy region at lower temperatures to its rubbery region at the higher temperatures.

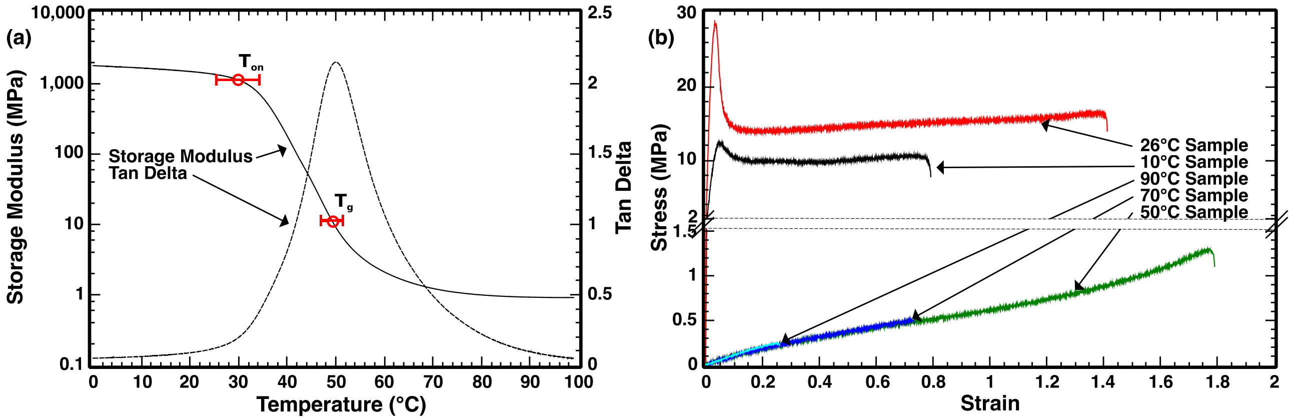


Figure 8: (a) Representative DMA curve of final ternary network along with the average T_{on}, T_g of the tests. (b) Tensile stress strain behavior as a function of temperatures tested over the glass transition region.

Additional test results found an onset temperature of 29.8±4.4°C and a glass transition temperature of 49.2±2.2°C, which are represented on the storage modulus curve in the figure. Note the modulus at five different temperatures that are used in tensile tests displayed in **Figure 8 (b)**. These points are tabulated in **Table 1** highlighting the orders of magnitude decrease in stiffness over the transition region.

Table 1: Average sample storage moduli, ultimate tensile strength, and strain to failure at various temperatures.

	Storage Modulus (MPa)	Ultimate Tensile Strength (MPa)	Strain to Failure	Toughness (kJ/m^3)
10 °C	1405±437	14.22 ± 2.80	0.600 ± 0.182	4,830 ± 3,120
26 °C	916±386	19.65 ± 6.95	1.405 ± 0.084	17,240 ± 5,220
50 °C	7.13±3.08	0.934 ± 0.469	1.607 ± 0.267	688 ± 430
70 °C	1.130±0.150	0.480 ± 0.063	0.872 ± 0.162	200 ± 52.7
90 °C	0.810±0.350	0.139 ± 0.094	0.1749 ± 0.0781	15.85 ± 16.30

The five temperature regions mentioned above were examined due to their location in the glassy-to-rubbery transition region. First well into the glassy region at 10°C, next at room temperature of ~26°C - close to the onset temperature, then at the glass transition temperature of 50°C, and rounded off at 70°C and 90°C which have transitioned fully into the rubbery region of the material.

As the material transitions from it glassy to rubbery regime, its mechanical properties are also expected to change. These transitions can be seen in the representative stress-strain curves for each of the five temperatures displayed in **Figure 8 (b)**. Results of strain to failure and ultimate tensile strength are additionally tabulated as a function of temperature in **Table 1**.

In **Figure 8 (b)** as well as **Table 1** note the large change in the materials mechanical behavior as temperature transitions from high to low both in ductility and ultimate strength, as well as overall behavior. There is a fundamental change in characteristic behavior between the 50°C and 26°C, the glass and onset temperatures respectively.

6.4 Molding Techniques

A large emphasis in this project was placed into development of an adequate soft molding technique, as the uncured acrylate system was found to absorb, at least to some degree, into a variety of silicone molding materials, including Silastic® 7-4860 silicone elastomer, Sylgard® 184 silicone elastomer, and Xiameter® RTV-4251-S2 silicone mold making rubber. All three of the silicones selected had various different advantages and disadvantages, and through experimentation the best solution was found involving a multi-step processes starting with a Delrin custom machined negatives of the structured surface (or master mold), Silastic elastomer, and finally followed by a Xiameter mold making rubber.

The soft molding technique can be better understood through observing **Figure 9**, where the six steps are shown from left to right. The first frame of the Figure, (a), displays a model of the prepared Delrin mold. Represented in frame (b) is Silastic- colored blue in the figure - which is supplied in extremely viscous two part base constituents that are mixed in equal parts to start the chemical polymerization of the substance. Stain-to-failure tensile testing comparing Silastic and Sylgard showed a much higher material toughness in Silastic, allowing for a more robust product during positive-negative mold delamination.

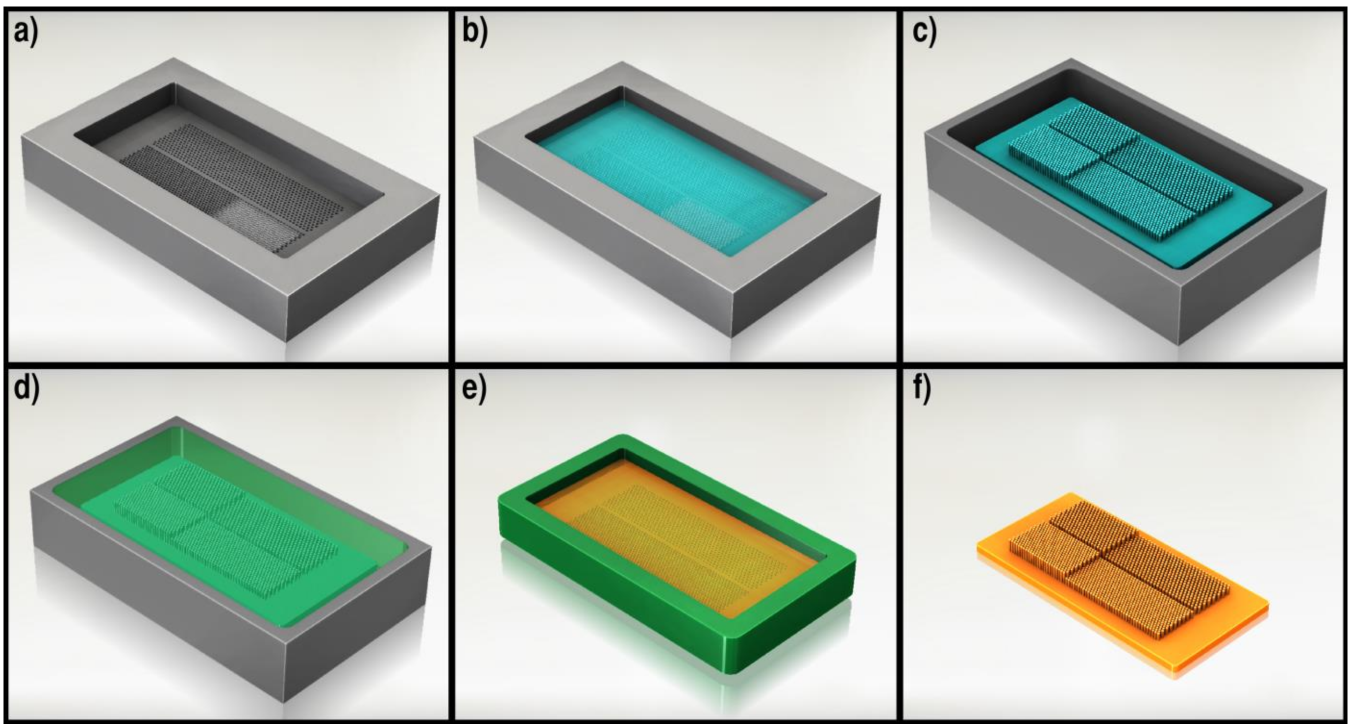


Figure 9: Soft molding process of acrylate structured surface. The Delrin master mold in (a) is (b) cast with Silastic creating an intermediate positive (c). After surface treatment, another silicone substance is poured and cured (d) creating a clone (e) that can be used to cure the final acrylate structure shown in (f).

As seen in frame (c), once the Silastic positive was demolded, it was placed in a custom dish that maintained the footprint of the positive, and added deeper walls that would ultimately allow for pouring the acrylate system into the Xiameter negative. Because both the Silastic and the Xiameter are silicon based materials, a release agent was necessary between the positive and negative molds. 11 mL of a Trichloro(1H,1H,2H,2H-perfluorooctyl)silane (PFOS)/Hexane solution (ratio 1:10) was placed in an open dish next to the sample and vacuum desiccated to approximately 380 Torr, sealed, and left for one day in order to be vapor deposited, creating a self assembled monolayer on the Silastic surface. The monolayer was then annealed at 150°C in an open-air furnace for one hour.

Immediately after vapor deposition of the release agent for 1 day, Xiameter was mixed in at 10:1 weight ratio of base to curing agent with a stainless stir rod and poured onto the Silastic mold and dish; represented by the green material in (d). The material was degassed and cured at 150°C for one hour. This method allowed for a good de-lamination between the Silastic positive and Xiameter negative.

With the welled Xiameter negative, the ternary acrylate network could finally be cast into the structured surface as is displayed in (e). Before casting, the polymer system was pre-cured using a 254 nm wavelength crosslinking oven for 15 minutes. The mixture was then poured in it the Xiameter mold, degassed for one minute, and photopolymerization was completed using a the 365 nm wavelength UV lamp for 15 minutes and placed in the oven at 90°C for 60 minutes. This process ultimately provided the final structured Acrylate surface seen in (f).

However, an alternative molding process involved moving directly from the Delrin master mold straight to the acrylate system. Although direct molding into the master negative was a higher risk operation with potential for permanently plugging the master mold, it proved more effective for creation of small section test samples, allowing for accurate delamination between both parts in a less time intensive process when compared to the soft molding techniques. Masters could typically be used approximately five times before deforming too much from the curing process, or being damaged with too much residual acrylate, requiring a new mold. The process described below is represented in **Figure 10**.

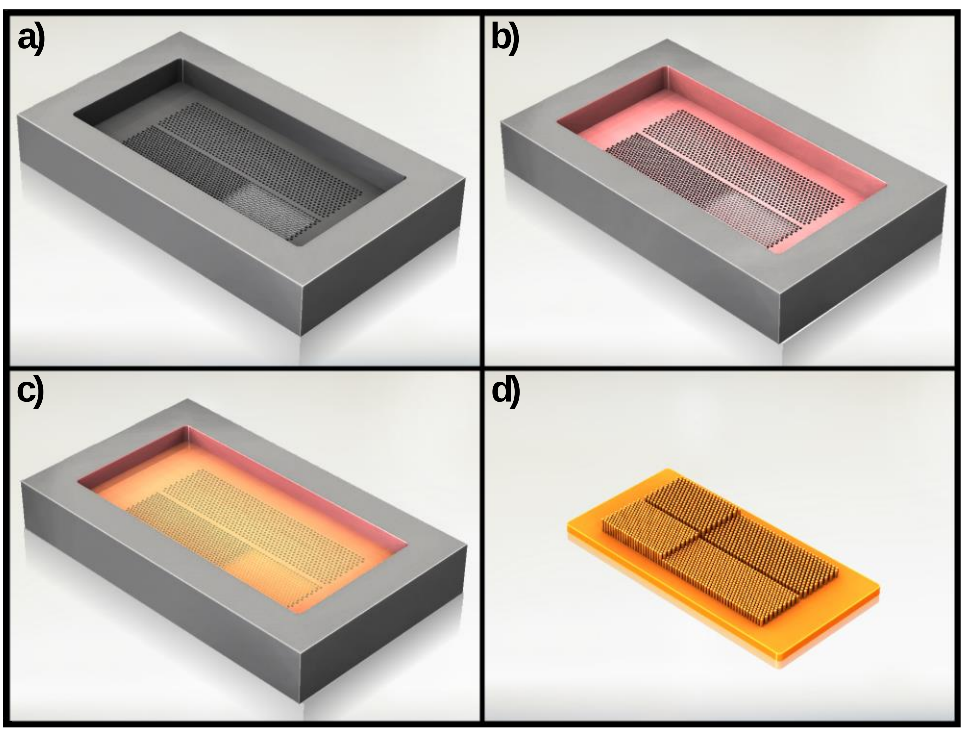


Figure 10: Direct molding process of acrylate structured surface. An (a) untreated Delrin mold is coated with an annealed monolayer of PFOS (b). In (c) the acrylate could be cast directly into the material and cured producing the final product (d).

To ensure the acrylate network would not adhere to the Delrin (a), molds first needed to be coated with a self-assembled film to act as a release agent, PFOS, shown in (b). A 10 mM solution of PFOS in Hexane was poured into the mold, placed in the refrigerator, and after 20 minutes, samples were removed from the solution and rinsed heavily with Hexane to remove any loosely bonded self assembled layer. Samples were finished curing in an open-air furnace at 150°C for 60 minutes, annealing the coating. With the self-assembled coating polymerized on the mold surface, represented as the red coating in the Figure, the final ternary polymer structure could be cast in frame (c). The acrylate was first pre-cured in a 254 nm wavelength crosslinking oven for 20 minutes, placed in the mold, degassed, finished polymerizing under a 365 nm wavelength UV lamp for an additional 10 minutes, and subsequently placed in an oven at 90°C for 60 minutes. The method allowed for simple delamination from the mold at elevated temperatures. Typically a direct molding process would be improbable, as their needs to be a large difference in elastic modulus between the mold and the product, hence the usual use of soft molding. However the acrylate has the benefit of becoming rubbery upon heating to assist in removal here, working excellently on the small scales here.

6.5 Surface Modification

Various methods of surface treatments could be employed to alter the wettability of the surface of the acrylate, regardless of the acrylate's water absorption characteristics. Ultimately, this could allow for different surface characteristics at various points in the structured pillared surface, creating a switchable properties. Three methods were investigated including Polydopamine coating (PDOPA), Trichloro(1H,1H,2H,2H-perfluorooctyl)silane coating (PFOS), and dip coating of Sylgard 184 silicone elastomer (PDMS).

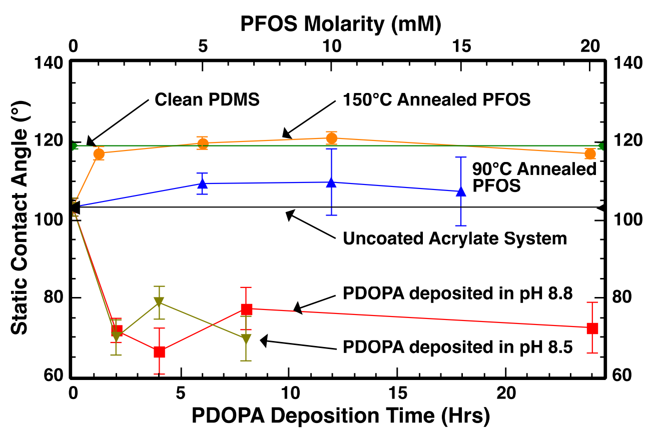


Figure 11: Contact angles of surface treatments applied to the final acrylate system.

Figure 11 displays the mean and one standard deviation of static contact angle results of PDOPA and PFOS surface coatings on flat sheets of the final acrylate system after soaking in ultra-pure water for 24 hours from a sample size of five to seven. These can be compared to results of pure PDMS and the final acrylate system's static contact angles with no variation in their material properties. PDOPA varied both deposition time as well as the pH of the deposition medium, and corresponds to the bottom axis. PFOS observations were made altering the solution concentration and annealing temperature, corresponding to the top axis. Note all PDOPA and PFOS results start with the uncoated Acrylate material contact angle of 103.3 ± 2.3° that was to be modified.

From the figure, it appears there is little difference between a deposition pH of 8.5 and 8.8 in the PDOPA coating process, though there is a large amount of variation in the initial process around 4 to 8 hours. Average results at 24 hours for a pH of 8.5 are 72.4 ± 6.5°, and are expected to be similar for a pH of 8.8.

The two curves of PFOS, annealed at different temperatures, follow the same trend being slightly optimized between a 5 and 10 mM deposition concentration, while decreasing a small amount at 20 mM. The importance of annealing temperature is also highlighted in the curves as the contact angles of a 10 mM solution increases from 109.7 ± 8.5° to 121.0 ± 1.6° with an increase in temperature from 90°C to 150°C. Therefore, PFOS can be considered similar to the pure PDMS sheets of 119.0 ± 0.8°. Results of pure PDMS complement results from Jin et al. static contact angles at 113° [5].

6.6 Combined Structured Surface

With investigation of all facets of the research complete, the structure surface could finally be combined, showing a proof-of-concept design. Pillared surface were first subjected to PDOPA treatment polymerized in a pH solution of 8.5 for 24 hours, leaving a mainly hydrophilic surface coating. The pillar tops were then either dipped in PDMS and cured, producing a hydrophobic flanged top, or placed in a PFOS bath, creating a self-assembled monolayer that was also very highly hydrophobic. Qualitative results with close ups of the final structured surface coated with various surface treatments in contact with water droplets are displayed in **Figure 12**. For the images, samples were presoaked, and subsequently dabbed to free surface water before placing a water drop on top.

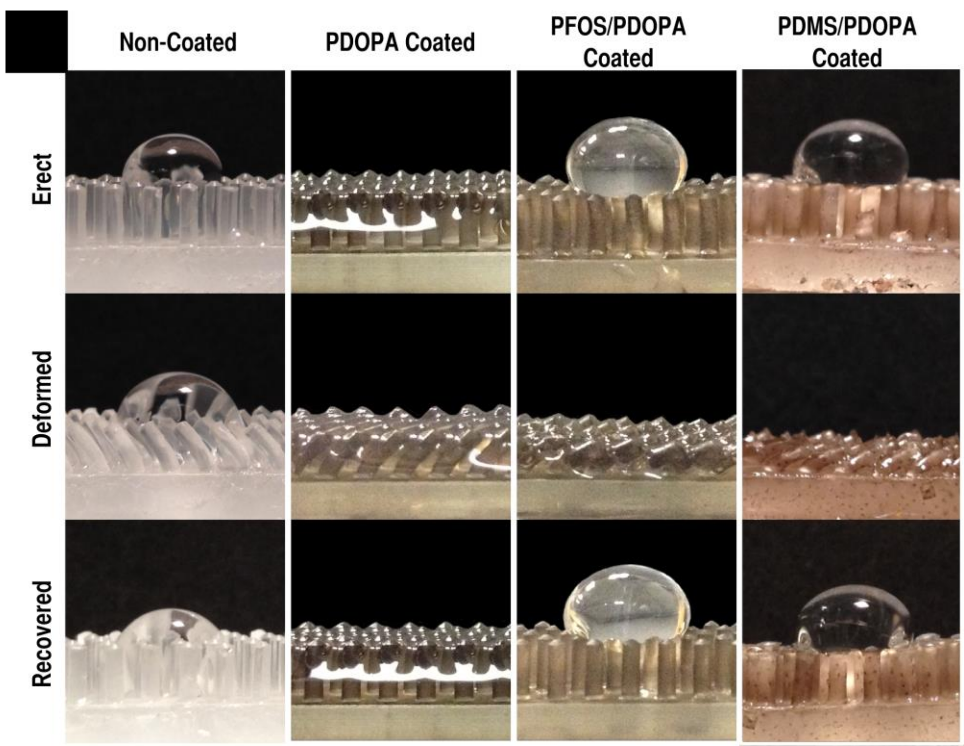


Figure 12: Qualitative results of water droplets in contact with structured acrylate system with various surface coatings (columns) in erect, deformed, and recovered conditions.

Columns from right to left include the non-coated structured acrylate system, PDOPA coated throughout, PDOPA coated with PFOS topping, and PDOPA coated with flanged PDMS pillar tops. The first row displays the material in the original un-deformed state, the second in the deformed state, and the third in the recovered state. Results qualitatively show the switchable hydrophobic effects, when using a combination of the pillar structure with surface treatments. Noting the first column, it is important, at least on the size scale here, that surface treatments are key for the switchable hydrophobic effect. The last two columns exemplify this characteristic, where the water (and any type of fouling material) is exposed to the hydrophobic tops, it displays hydrophobic behavior, but when relaxed, the pillars expose the hydrophilic surface, dispersing the water. This can then be returned to its original state.

7 Discussion / Significance:

A proof-of-concept, switchable hydrophobic, structured surface was created in this research, with an ultimate targeted application acting as assistance to antifouling in pressure driven water treatment membranes. This was done through a multi-tiered design using a patterned shape memory polymer with selectively treated surface locations, inducing a hydrophobic of hydrophilic effect.

A majority of the research presented here focused on investigation and design of a custom tailored shape memory polymer that could be cast into a structured surface. The final composition of this ternary acrylate polymer consisted of 94.5/ 5.0/ 0.5 wt.% linear building mixture of 9:1 tBA:2HEMA, PEGDMA550, and DMPA, or a final relative weight percentage of each constituent overall of 85.05/ 9.45/ 5.00/ 0.50 wt.% tBA, 2HEMA, DEGDMA, and DMPA. The polymer was optimized for good shape memory properties in a targeted temperature range, water absorption characteristics, and applicable thermo-mechanical properties. Final glass transition and onset temperatures were 49.2±2.2°C and 29.8±4.4°C respectively.

The second stage focused on developing the basis for a structured surface. Emphasis was placed on research-scale manufacturing processes to cast patterned structured surfaces as well as application of hydrophilic and hydrophobic surface treatments, and how to selectively locate them on the cast surface. A manufacturing method for the surfaces at the research scale was not immediately apparent, taking a large amount of research, though in the end two processes emerged. This included a soft molding process as well as a direct molding process, which both had there advantages and disadvantages depending on the requirements of the final product.

Thirdly, this project developed a reliable method of altering surface properties especially along the cast pillar surface through the use of PFOS, PDMS, and PDOPA. The major advantage to altering surface characteristics is that the underlying structure can remain the same, while locally the material can be made hydrophobic or hydrophilic. It is through the combination of the materials geometry, as well as the surface characteristics that we can see the stark change in the apparent hydrophobicity of the surface, as seen in the final figure, **Figure 12**.

Through this funding, significant progress was made into the novel surface, laying the groundwork that can be built upon with additional work. We have show through proof-of-concept the framework for a switchable surface including a custom designed acrylate system, appropriate molding techniques, and application of surface treatments that can easily be spatially modified. Future work can therefore build upon this design, taking it to a smaller scale, optimizing the geometrical patterning and direct fouling testing. However, the steps taken here are significant strides towards a surface that will, in the future, aid in membrane filtration processes.

8 Project Publications:

8.1 Thesis

C. M. Laursen, “Proof-of-concept switchable hydrophobic/hydrophilic patterned surfaces from thermo-mechanically tailored acrylate systems,” M.S. thesis, Dept. Mech. Eng., Univ. of Wyo., Laramie, WY, 2014.

8.2 Publications

A paper is being prepared for submission to *Surface and Coatings Technology*, summer 2015.

9 Student Support and Training:

Graduate:	Christopher M. Laursen, M.S. Mechanical Engineering 2014
	Anthony J. Hoyt, M.S. Mechanical Engineering 2015
Undergraduate:	Samuel R. Gates, B.S. Mechanical Engineering 2014
	Aidan H. McDonald, B.S. Mechanical Engineering exp. 2016

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Use of Fe(VI) for the Improvement of Water Quality in Wyoming

Basic Information

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Principal Investigators:	Maohong Fan, Lamia Goual

Publications

1. Tuwati, Abdulwahab M. Ali., New Technologies for Dealing with CO2 Emission and Carbonate Discharge Control Issues Associated with Energy Production, Ph.D. Dissertation, Department of Chemistry, University of Wyoming, December 2013, 100 pgs.
2. Dong, S., Feng, J., Fan, M., Pi, Y., Hu, L., Han, X., Liu, M., Sun, J., 2015. Recent Developments in Heterogeneous Photocatalytic Water Treatment Using Visible Light-responsive Photocatalysts: A Review, RC Advance, Vol. 5, PP. 48901-48904.
3. Irani, M, Ismail, H., Ahmad, Z., Fan, M., 2015. Synthesis of Linear Low-density Polyethylene-g-poly (Acrylic Acid)-Co-Starch/Organo-Montmorillonite Hydrogel Composite as an Adsorbent for Removal of Pb from Aqueous Solutions, Journal of Environmental Sciences. Vol. 27, No.1, PP 9-20.
4. Sharrad, O. M., Fan, M., 2015. Adsorption of Carbonate and Bicarbonate on FeOOH, International Journal of Advanced Technology in Engineering and Science, Vol. 3, No. 1, 2348-7550.

Use of Fe(VI) for Removal of Total Organic Carbons (TOC) and Heavy metals from Coproduced Water in Wyoming

Annual Report

(Year 2 of 3)

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Abstract

The objective of the research is to develop a new, simple, and environmentally friendly method for the simultaneous removal of heavy metals and total organic carbon (TOC) in coproduced water (CW) from the energy production industry. Ferrate anions (FeO_4^{2-}) or Fe(VI) oxidation ability is very strong over the whole pH scale. Fe(VI) has been considered one of the future-generation water quality improvement agents. The oxidation of CWs TOC into CO_2 and H_2O can be done via Fe(VI). The result of the reduction of Fe(VI) is Fe(III) which is an excellent adsorbent for removal of heavy metals in CWs. Once the heavy metals and TOC have been removed from the CWs it is much easier to then remove the total dissolved solid (TDS) from the CWs. Water supply around the world is becoming insufficient for the growing populations and sources for additional water supplies must be established. Treated CWs can potentially be used to partly mitigate the tight water supply dilemmas in states such as Wyoming.

1. Description of Proposed Research

Wyoming is widely considered to be in a semi-arid hydro-climatic region. A vast majority of the time, rivers and streams throughout the state have little flow, granted during rare events, these rivers and streams can swell to very large levels. Wyoming has limited sustainable surface water available for use in general. Furthermore natural disasters such as droughts and tornadoes can suddenly scourge some regions of Wyoming by undermining agricultural and industrial productivity as well as the well-being and social fabric of communities. Point and nonpoint pollution is a manmade disaster that has been a long-standing concern that may further weaken Wyoming's capability to reach its water requirements. It is vital that Wyoming will not be threatened indefinitely due to a lack of water resources. In response to the water crisis, Wyoming statute Title 35, Chapter 11, Article 3 (35-11-309) declares "water is one of the Wyoming's most important natural resources, and the protection, development and management of Wyoming's water resources is essential for the long-term public health, safety, general welfare and economic security of Wyoming and its citizens." Wyoming mining and energy production companies have generated a great deal of water known as coproduced water (CW). These CWs regularly contain difficult to remove inorganic heavy metals and organic compounds whose disposal will not only cause serious environmental problems, but also waste the precious water resources that are desperately required in Wyoming. Consequently, treatment of CWs for use in Wyoming is a win-win approach.

CWs from various energy production industries [1] have been considered as important new water resources. Nonetheless some of the CWs need to be treated due to quality issues including heavy metals, total dissolved solids (TDS), and high total organic carbon (TOC) associated with fossil fuels [2-3], natural gas and coal. Removal of heavy metals and TOC can greatly help facilitate TDS reduction and removal. Presently there are two separate steps and two different technologies to remove heavy metals and TOC. The first step is to remove the TOC. TOC can be degraded through biological processes that are environmentally friendly, but slow [4]. TOC can also be destroyed using UV photolytic [5] and electrochemical [6] methods, but they are expensive and difficult to control. Most recently a combination of the methods has been studied [7-10] to achieve high removal efficiencies of TOC with some progress being made, however these processes are complex. To overcome these downfalls of a multistep method efforts have been put into using a simple multifunctional technology for simultaneous removal of the organic compounds and heavy metals to improve the overall CW quality of Wyoming. Specifically, a proprietary green method to produce a multifunctional K_2FeO_4 (simply called Fe(VI) henceforth) and propose to use it for the simultaneous removal of total organic carbons (TOC) and heavy metals in numerous CWs preceding their further treatments for total dissolved solids (TDS) removal with other technologies such as reverse osmosis.

Success in this project will benefit water resource conservation, environmental quality protection, and agricultural and energy development. These benefits will be accomplished with the following results. Firstly, the optimal Fe(VI) quality for removal of TOC and heavy metals in CWs will be established. Second, the operation conditions for the proposed CW contaminant removal technology will be obtained from laboratory bench-scale data collection. A TOC analyzer will be used to find the concentrations of TOC before and after treatment to determine the effectiveness of Fe(VI) on removing TOC from the CWs. The concentrations of heavy metals will be measured before and after treatment with an inductively coupled plasma mass spectrometer (ICP-MS) to determine the performance of Fe(VI) in removing the heavy metals. Lastly, to demonstrate the applicability of the proposed technology, a pilot-scale test set-up will be designed and built based upon test results from the laboratory bench-scale setup. The results from the pilot-scale set-up are expected to reveal the operation conditions needed for use of the proposed technology in industry for future use. Studies in the use of Fe(VI) have not been done for its application in CW treatment, but it has for other water treatments. Success in the proposed project will advance the application of Fe(VI) in the energy industry as well as other industries working with organic compounds and heavy metals.

Ferrate anions (FeO_4^{2-}) or Fe(VI) oxidation ability is very strong over the whole pH scale. Fe(VI) has been considered one of the future-generation water quality improvement agents. The oxidation of CWs TOC into CO_2 and H_2O can be done via Fe(VI). The result of the reduction of Fe(VI) is Fe(III) which is an excellent adsorbent for removal of heavy metals in CWs.

2. Tasks

Task 1 includes building the laboratory setups seen in Figure 1 and Figure 2. The first step for treatment of CW will be to add 1 L of collected CW to the vessel followed by turning on and setting the stirrer to the desired speed. The temperature control unit will then be turned on to control the operating temperature (5, 10, 15, 20, or 25 ˚C) depending on the test. Next a chosen amount of Fe(VI) will be added once the CW reaches the desired temperature. The reaction will be conducted for a predetermined amount of time with samples being taken periodically to monitor TOC and heavy metal concentrations during the reaction.

Task 2 includes analyzing the samples from the as-received CWs as well as the CWs treated with Fe(VI) under varying conditions. A TOC analyzer will be used to measure the concentrations of TOC and an ICP-OES will be used to measure the concentrations of heavy metals. Other water quality parameters such as suspended solids (SS), total dissolved solids (TDS), electrical conductivity (EC), and pH values of CWs will also be monitored using corresponding instruments available on UW campus. Also, the concentrations of Fe(VI) solution used to treat the CWs will be determined using UV spectroscopy.

Task 3 is the performance evaluation of Fe(VI) on the removal of TOC and heavy metals from CWs on the bench-scale set-up under different conditions. These tests will be used to investigate the TOC and heavy metal removing efficiencies of Fe(VI) under different CW conditions including TOC and heavy metal concentration levels, SS, pH, TDS, temperature, stirring speed and Fe(VI) dosage. The major organic compounds (major TOC contributors) in the CWs will be identified, as well as the kinetics associated with reactions between major organic compounds and Fe(VI).

Task 4 will be to test if the sludge resulting from treatment of CW with Fe(VI) is stable when landfilled. The TOC is expected to be completely decomposed into CO_2 and H_2O when the optimal treatment conditions and dosage of Fe(VI) are used. So, this task is designed to evaluate the stability of heavy metals in the sludge using EPA SW-846 Method 1311 (Toxicity Characteristic Leaching Procedure (TCLP)). The optimal CW treatment conditions for achieving the greatest heavy metal stabilities in sludge will be investigated.

Task 5 is to perform industrial/commercial-scale demonstration of the proposed CWs management technology based on the results achieved with bench-scale tests. The volume of the batch vessel will be scaled to up to 1,000-2,000 L. The on-site industrial/commercial-scale demonstrations will be done in one of oil or natural gas production companies. The specific location of the project will be determined by discussing with the associated landowner and oil/gas companies. Less than 0.5 acre of land will be used for pilot-scale and industrial/commercial-scale demonstrations of the proposed technology. The quality parameters (including TOC and heavy metal concentrations, pH, SS and TDS) of the as-received CW from the chosen company will be characterized. The data obtained from bench-scale tests will be used as the references of the industrial/commercial-scale tests. Factorial tests will be done to assess the performance of Fe(VI) on CWs treatment at industrial/commercial-scale.

3. Methods

3.1 Jar tester

A photo (Figure 1) shows the PB-700 jar tester that is being used for water sample mixing. It is equipped with six stainless steel 1" x 3" paddles which are spaced six inches apart and are adjustable to a maximum depth of nine inches. An electronic motor control system offers regulated variable speeds of all paddles simultaneously, from 1-300 rpm, with the exact speed clearly displayed on a digital readout. A fluorescent lamp illuminator is built into the jar tester base to provide soft, diffused lighting of samples being tested. This setup is used in the first part of this project and the final analysis of water samples are analyzed via Total Organic Carbon (TOC) analyzer.

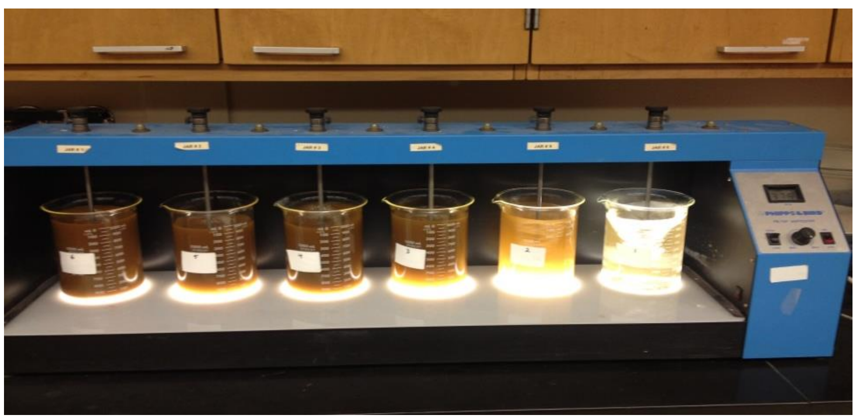

Fig. 1 Photo of the jar tester setup

3.2 Glass reactor

A comparative laboratory scale set-up that will be used to remove TOC and heavy metals from CWs with Fe(VI) is schematically illustrated in Figure 2. Each of the experiments will be executed in a 1 L stirred glass vessel (5). The glass vessel will have five inlets through its lid. In the center inlet of the glass lid a Teflon shaft with a propeller will be inserted (6). The next inlet will be used to introduce CWs and Fe(VI) into the vessel (4). A thermometer will be inserted into another one of the five inlets (7) to monitor the temperature that will be controlled by a separate temperature control unit (3). The fourth inlet will be used to introduce nitrogen when needed to increase the efficiency of mixing in the vessel, which will be controlled by a rotameter (2). A condenser (8) will be connected to the last inlet to condense any vapor released from the reaction mixture and return it to the vessel. The condenser regulating unit (9) will be used to control the condenser temperature. A sampling port will be fitted at the bottom of the vessel as can be seen in Figure 2.

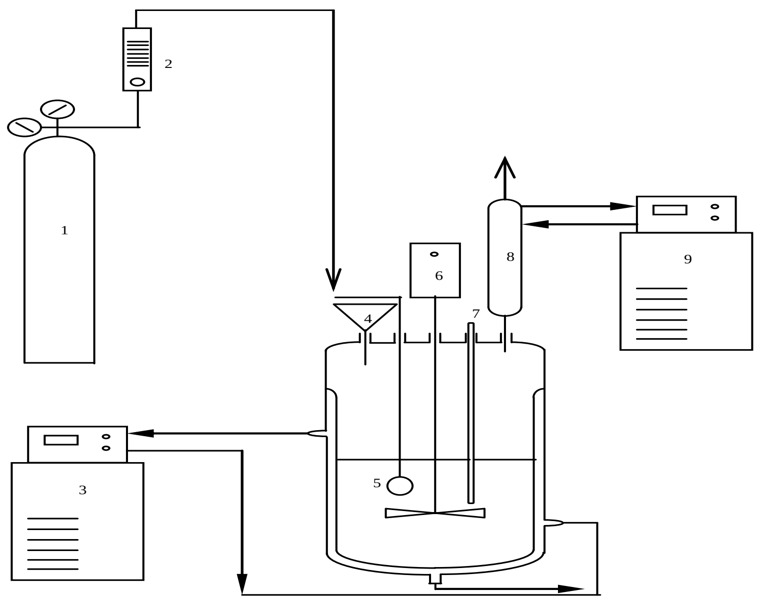

Fig. 2 Experimental setup for removal of TOC and heavy metals from CWs with Fe(VI) [(1) nitrogen tank (2) rotameter (3) temperature control unit (4) funnel (5) vessel (6) stirrer motor (7) thermometer (8) condenser (9) condenser regulating unit]

4. Progress

4.1 Fe(VI) Synthesis

In accordance to task 1 the first set-up as seen in Figure 1 is currently running and being used for experiments. Original results have shown that TOC was not being removed effectively. To determine the source of this problem the Fe(VI) that had been used was tested using Mössbauer spectroscopy. The results from this have shown that our original Fe(VI) samples were less than two percent of the Fe(VI) oxidation state, with the rest being Fe(III). To overcome this difficulty we had decided to produce our own Fe(VI) samples. To complete this we have developed a process of oxidizing Fe(III) into Fe(VI) using ozone. The solid preparation method has been realized through the reaction seen in R1.

$$2FeOOH + 4KOH + 3O_3 \rightarrow 2K_2FeO_4 + 3H_2O + 3O_2 \qquad R1$$

Fe(VI) preparation consists of two principal steps. First the loading of KOH onto the surface and pores of FeOOH through adsorption is completed to prepare the reactants. Next, oxidation of the reactant complex by ozone is done to produce potassium ferrate. The setup for preparation of Fe(VI) can be seen in Figure 3. The first step consists of measuring a quantity of FeOOH and introducing it into a KOH solution. Next this mixture was slightly heated to about 60 ˚C and simultaneously stirred for one minute. The resulting solution is then placed into and oven at 90 ℃ to evaporate the water from the solution. Once dried the complex (FeOOH+KOH) was then placed in the fluidized bed reactor. Step two consists of the following stages. Ozone is produced from oxygen by an ozone generator and streamed into a humidifier containing distilled water. The humidified ozone is then fed to fluidized bed reactor to oxidize the KOH FeOOH complex. Glass wool is used to retain the reactants in the reactor. The reaction product is a dark purple powder containg a proportion of potassium ferrate and unreacted reactant.

4.2 Fe(VI) Analysis

4.2.1 Spectrometry

At the end of the reaction the solid product purity is measured using a UV/vis spectrophotometer. The solid product is filtered with a large quantity of deionized water. This filtrate is what is measured using the UV/vis spectrophotometer at 510 nm. Molar absorptivity at 510nm had been determined previously as 1150 M^{-1} cm^{-1} by Bielski and Thomas (1987), based on the Beer-Lambert law as shown in the equation A=εbc, in which "A" is absorbance (no units, since $A = \log_{10} P_0 / P$); "ε" is molar absorptivity, with units of L mol^{-1} cm^{-1}; "b" is the path length of the sample (i.e., the path length of the cuvette in which the sample is contained, expressed in centimeters); and "**c**" the concentration of the compound in solution, expressed in mol L^{-1}. The determination of the molar absorptivity of the ferrate and the immediate measurement of the filtrate with the spectrophotometer gives the absorbance of light by Fe(VI). This value can then be used to calculate the concentration of Fe(VI) in the product through the equation E1.

$$Conversion = \frac{\left(\frac{Abs}{1150 \times 1}\right) \times 56 \times Vol(filtrate)}{Iron(content) \times FeOOH(weight)} \qquad \text{E1}$$

Abs is the value from the spectrophotometer, Vol(filtrate us the volume of deionized water used in the filtration, expressed in L. Iron(content) is the proportion of iron contained in the FeOOH used for the reaction, FeOOH(weight) is the weight of FeOOH used for the reaction in grams, and last the 1=1cm for the path length of the cuvette used in the spectrophotometer. 10% conversion is current maximum we have achieved with the current set-up. Optimization will be completed.

4.2.2 Titration

The previous analysis of Fe(VI) purity in potassium ferrate only works for samples that were made in the lab. K_2FeO_4 has also been bought from a chemical company. To determine the purity of this Fe(VI) another method is needed. A method from J.M. Schreyer of the University of Kentucky [12] will be used. This method is based on the oxidation of chromite in strongly alkaline solution with the ferrate(VI) ion as shown in reaction R2.

$$CrOH_4^- + FeO_4^{2-} + 3H_2O \rightarrow Fe(OH)_3(H_2O)_3 + CrO_4^{2-} + OH^- \qquad R2$$

This method is applicable to the analysis of solutions containing low concentrations of the ferrate(VI) ion. The procedure is as follows. First saturated sodium hydroxide is added to a chromic chloride solution. To this the sample to be analyzed is added and stirred until dissolution of the potassium ferrate is complete. Dilution is then done with distilled water followed by addition of sulfuric and phosphoric acids. Titration is then completed with a standard ferrous solution and a sodium diphenylamine sulfonate indicator.

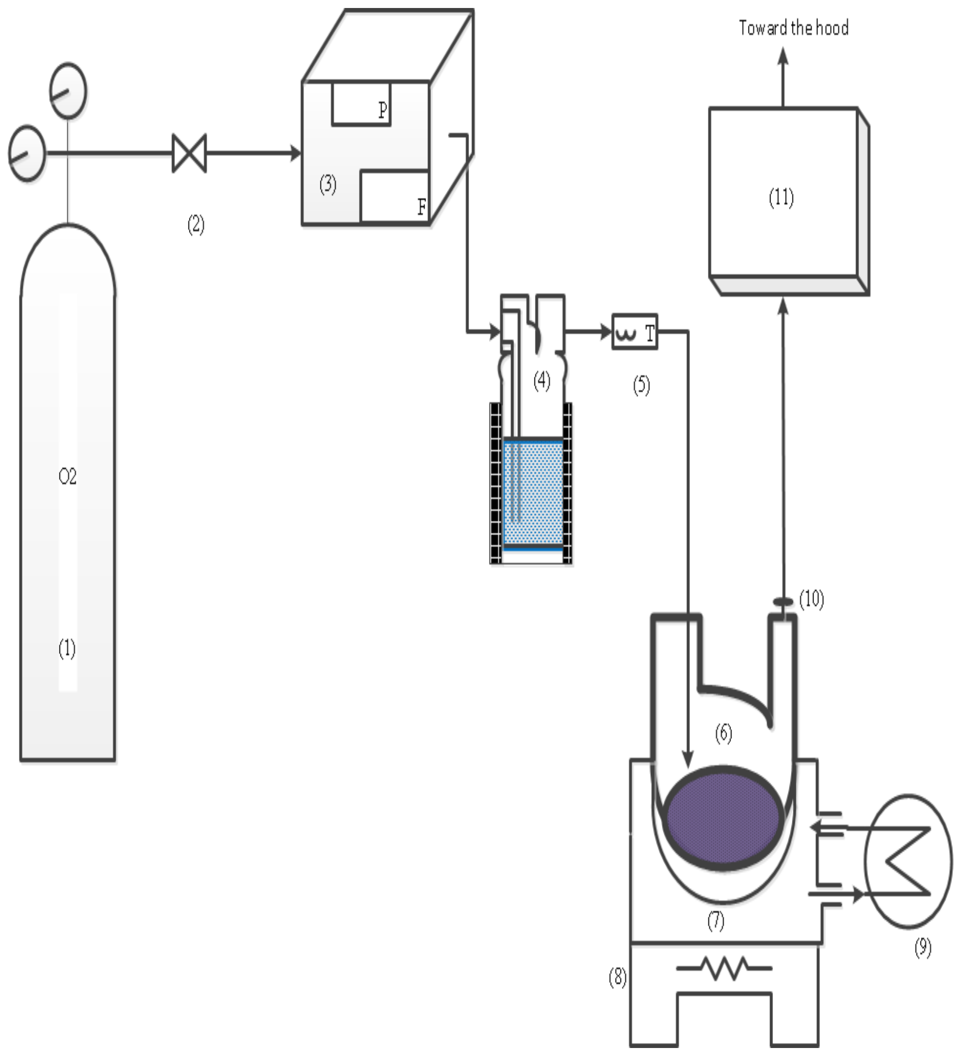

Fig. 3 Diagram of Fe(VI) preparation setup (1) Oxygen cylinder; (2) Valve; (3) Ozone generator; (4) Humidifier containing distilled water and heat tape; (5) Set of thermometers for wet and dry temperatures; (6) Fixed bed reactor containing FeOOH+KOH particle to be oxidized; (7) Jacket heat exchanger; (8) Magnetic stirring machine; (9) Temperature controller for heat exchanger; (10) Particle filter; (11) Ozone analyzer.

The end point is marked by a change from purple to light green. From the known amount used of the ferrous solution titrant the percent potassium ferrate can be calculated as seen in equation 2.

$$Percent\ K_2FeO_4 = \frac{(ml\ of\ Fe^{2+} * N\ Fe^{2+}) * K_2FeO_4\ MW}{3000 * m} \qquad \text{E2}$$

Where Fe^{2+} is the titrant solution used, N is nomal, MW is molecular weight, and m is the weight of sample used in the analysis.

4.3 Total Organic Carbon (TOC) Removal

Different components have been used for initial analysis of Fe(VI). Methanol, ethanol, ethanol amine, benzothiazole, and phenol have all been used due to their solubility in water. Reactions include variation of Fe(VI) dosage, pH variations, initial concentrations, and temperature. Phenol removal tests at varying initial Fe(VI) concentrations were completed. The reactions for the variation of Fe(VI) concentrations was done at a pH=5 for 15 min., an initial TOC concentration of 30 ppm, and a stirring rate of 250 RPM. It has been found that after adding more than 4 grams of Fe(VI) the percent of TOC removal plateaued, meaning the extra Fe(VI) did not oxidize anymore giving an optimal Fe(VI) concentration of 4 g/L as seen in Figure 4. This concentration of Fe(VI) was then used to measure the removal efficiencies at varying pH's. This data can be seen in Figure 5. Future reactions will be done at this value for maximum removal efficiency.

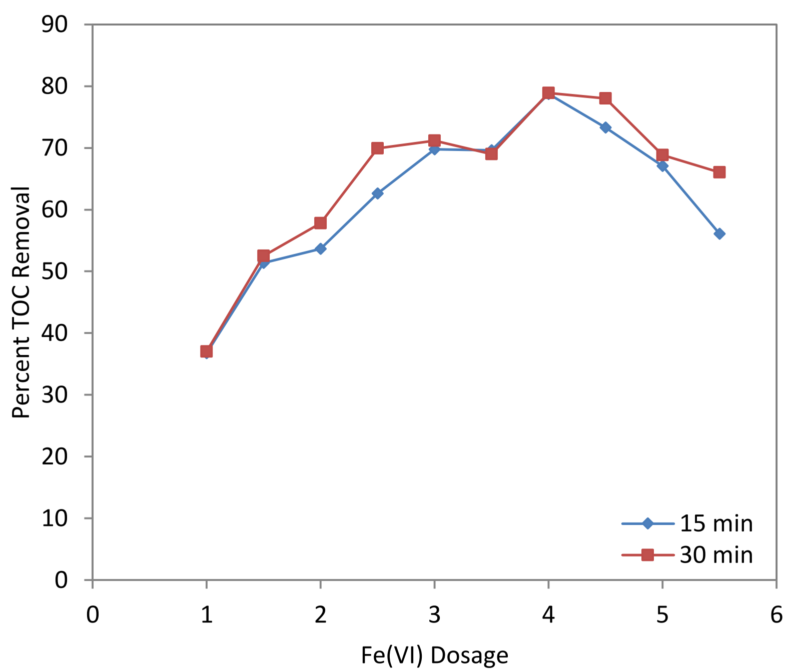

Fig. 5 Percent TOC removal at varying Fe(VI) concentrations. The initial concentration of TOC as phenol was 20 ppm with pH value of 5. The reaction was run for 30 min. at a stirring speed of 250 RPM with samples taken at the end of reaction and in the middle of the reaction.

Chemical oxygen demand (COD) analysis was also completed on the samples obtained from experiments. The same trend exists in COD removal as in TOC removal. The optimal pH of three and four can be seen in Figure 6 where 100% COD removal occurred. The pH of one was not able to be completed due to the reagents used in the COD analysis not being compatible to such a low pH value. Future work will find an alternative for this obstacle.

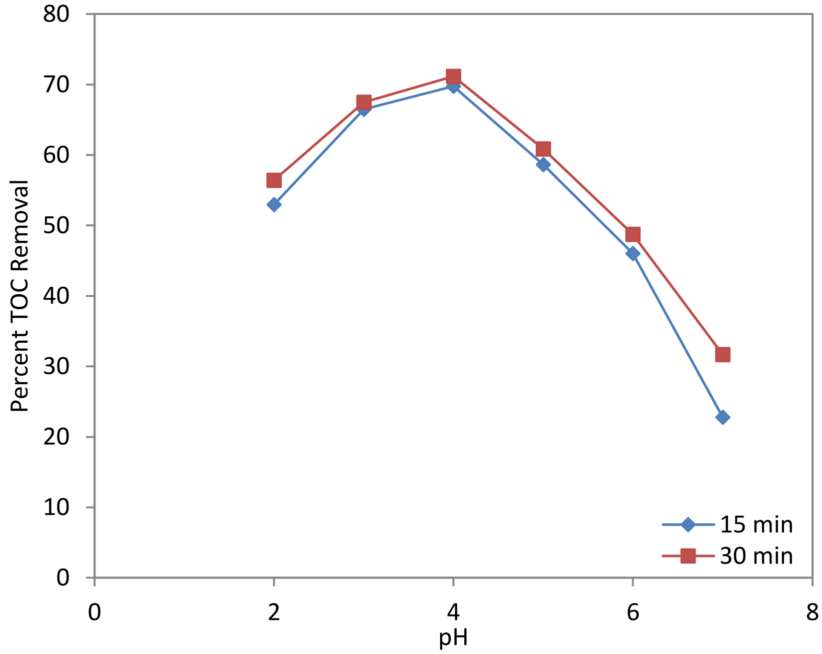

Fig. 5 Percent TOC removal at varying pH levels. The initial concentration of TOC as phenol was 20 ppm with an initial dosage of 4 g Fe(VI). The reaction was run for 30 min. at a stirring speed of 250 RPM with samples taken at the end of reaction and in the middle of the reaction.

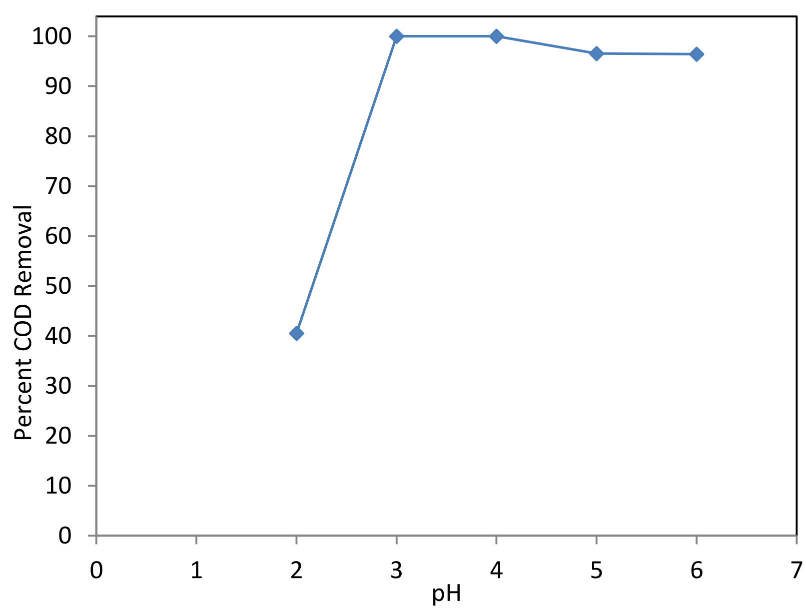

Fig. 6 Percent COD removal at varying pH levels. The initial concentration of TOC as phenol was 20 ppm with an initial dosage of 0.4 g of Fe(VI). The reaction was run for 15 min. at a stirring speed of 250 RPM.

Benzothiazole removal has also been studied. The same variation of conditions as seen in phenol removal has also been done. This includes varying of pH and Fe(VI) concentrations. It can be sen in Figure 7 that the optimal Fe(VI) concentration still has yet to be found as the removal efficiency is still increasing. Samples were taken at 15 and 30 minutes. There is no notable difference at Fe(VI) concentrations below 4.5 g/L, meaning the reaction has finished. Although above this concentration more removal is done at the 30 minute sampling time. This means with the higher Fe(VI) concentrations the reaction takes longer to finish, but more benzothiazole removal is achieved.

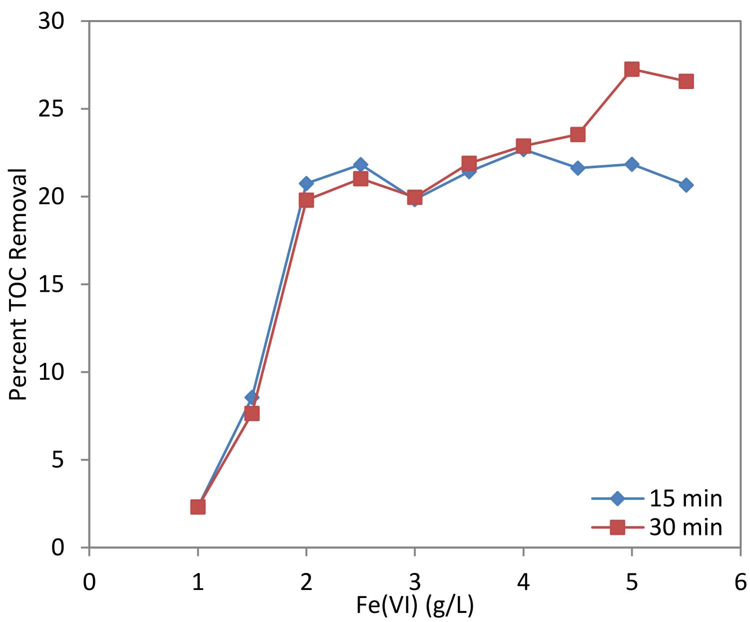

Fig. 7 Percent TOC removal at varying Fe(VI) concentrations. The initial concentration of TOC as benzothiazole was 15 ppm at a pH of 4.0. The reaction was run for 30 min at 250 RPM with sampling taken at the end and the middle of the reaction.

Variation of pH on benzothiazole removal after 15 min. can be seen in figure 8. For pH values of 2, 3, and 4 the samples that were taken at 30 minutes had no notable difference to the 15 minute samples. For the rest of the pH values the 30 minute TOC values actually increased instead of decreasing. The reason behind this is unknown and will be figured out in future work.

4.3 Analysis Methods

4.3.1 TOC Analyzer

TOC analysis requires that 20 mL samples of the treated water be introduced to a glass vial. These glass vials are then placed into the ASI-V Shimadzu auto sampler. A calibration curve is then set-up for the TOC analysis. Air zero is used as the supply gas for the TOC-V_{CSN} Shimadzu total organic carbon analyzer.

4.3.2 COD Analyzer

Small portions of the treated water samples were taken out for Chemical Oxygen Demand (COD) measurements via a colorimetric technique. Prior to the colorimetric determination of COD, specified amount of the samples were added into reagent vials containing dichromate solutions provided by Hach Co., followed by vigorous mixing and then placed in a pre-heated COD reactor for two hours at 150^{o}C. The vials were then cooled down to room temperature, removed from the reactor and then analyzed colorimetically via Hach DR/4000 instrument at a wavelength of 620 nm.

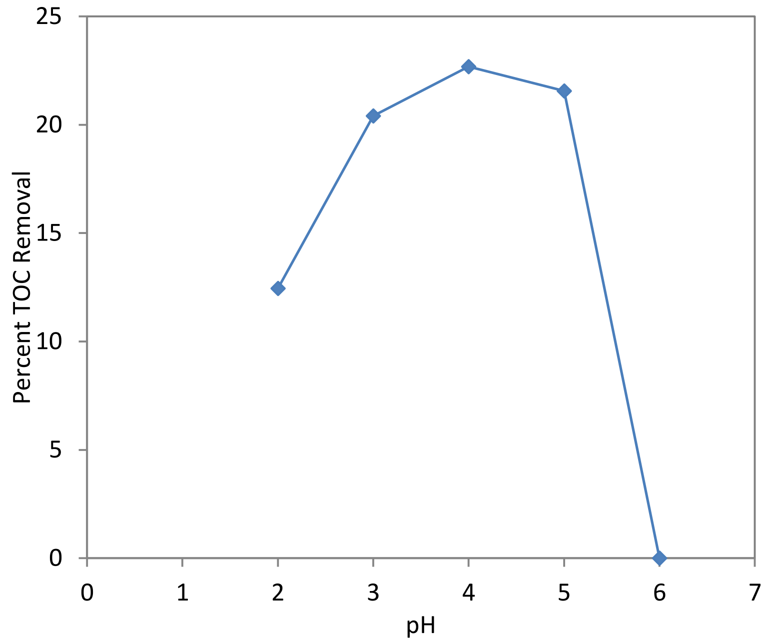

Fig. 8 Percent TOC removal at varying pH values. The initial concentration of TOC as benzothiazole was 15 ppm at a Fe(VI) concentration of 4 g/L. The reaction was run for 15 min at 250 RPM with sampling taken at the end of the reaction.

4.4 Parties Involved

The completion of this project has been assumed by Abdulwahab M. Ali Tuwati, a post doc with a PhD in chemistry, Andrew Thomas Jacobson, a Masters candidate in chemical engineering at the University of Wyoming, and Mohammad Tarabzoni an undergraduate student in chemical engineering at the University of Wyoming; all under the supervision of Professor Maohong Fan. The ideas behind the project have also been introduced to students through the GK-12 Environmental and Energy Nanotechnology NSF Fellowship through Andrew Jacobson. As a fellow, travel has been done to Chugwater, WY to introduce science topics including this ongoing research. Students from around Wyoming have also been given lab tours explaining the ideas behind the setups of this research and what the goal of this research is.

5. Future Work

Future work will contain a number of duties. First and foremost other molecules besides phenol and benzotialzole need to be investigated. This includes other compounds that contain aromatic rings like phenol which are considered to be harmful to the environment and the public health. Also removal of multiple contaminants simultaneously will be done. If possible more analyses will be completed using high performance liquid chromatography (HPLC) with a mass spectrometer to reveal the intermediate products created from the oxidation reactions with Fe(VI) along with the selectivity of Fe(VI) on the simultaneous removal of multiple contaminants. The method in synthesizing potassium ferrate from KOH and FeOOH will be optimized by varying initial conditions to give rise to higher Fe(VI) conversion. This higher conversion will be beneficial in that less Fe(VI) powder will need to be used in oxidation reactions. Once the Fe(VI) has been oxidized to Fe(III) for the removal of TOC there is still potential for the removal of heavy metals such as arsenic and selenium. This work will be completed once optimal conditions for the removal of TOC have been studied. Once the method has been validated for removal of multiple organic carbon types and inorganic molecules it will be applied to real water samples from various places in Wyoming. Currently we have set-up an arrangement with local companies to provide water samples from the energy industry.

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Rumen Microbial Changes Associated With High Sulfur A Basis for Developing Treatments for Ruminant Livestock in High Sulfur Water Regions

Basic Information

Title:	Rumen Microbial Changes Associated With High Sulfur A Basis for Developing Treatments for Ruminant Livestock in High Sulfur Water Regions
Project Number:	2013WY87B
Start Date:	3/1/2013
End Date:	2/29/2016
Funding Source:	104B
Congressional District:	1
Research Category:	Biological Sciences
Focus Category:	Agriculture, Treatment, Water Quality
Descriptors:	None
Principal Investigators:	Kristi Cammack, Kathy Austin, Gavin Conant, William Lamberson, Ken C Olson, Cody L Wright

Publications

1. Clarkson, Cara, 2014. Effect of high sulfur water on lamb performance and rumen microbial populations. M.S. Thesis, Animal Science, Univ. Wyoming.
2. Clarkson, C.J., H.C. Cunningham, L.E. Speiser, M.J. Ellison, K.J. Austin, and K.M. Cammack, 2014. Effect of high sulfur water on behavior, performance, and volatile fatty acid production in lambs. Proceedings Abstract, Western Section – American Society of Animal Science.

Rumen Microbial Changes Associated With High Sulfur – A Basis for Developing Treatments for Ruminant Livestock in High Sulfur Water Regions

Annual Report

(Year 2 of 3)

UPDATE: 05/01/2015

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Abstract: Reliable drinking water sources that meet minimum quality standards are essential for successful livestock production. Recent surveys have shown that many water sources, especially throughout the semi-arid rangelands of the U.S., are not of sufficient quality to support optimum herd/flock health and performance, in particular because of high concentrations of sulfur (S) and S-compounds present in the water. High S concentrations in water sources can arise from several factors. First, water sources can be naturally high in S. Second, drought conditions can cause S to be concentrated within the water source. Third, conventional oil and gas production can also increase S content within the water source. Combinations of these conditions can further exacerbate S levels in the water. Many of these water sources are used for livestock production systems, especially throughout the western states. However, high-S water is associated with poor performance and health in ruminant livestock, and is a primary cause of polioencephalomalacia (PEM), a disease state that can cause 25% morbidity and 25-50% mortality in affected populations. Producers are typically limited in available water resources and cannot avoid high S water situations; there are also no practical means of treating high S water. Although no effective treatments are currently available for animals suffering from the effects of high dietary S, it has been noted that animals vary in their response to elevated levels of S. While some animals consuming high S water exhibit reduced performance and/or poor health, others appear unaffected. We hypothesize that differences in rumen microbial populations, which are responsible for the breakdown of S and S-compounds, are associated with the variation in animal response to high S. Therefore, in this study we aim to 1) determine how rumen microbial populations change in response to high S water, and 2) determine if the extent of those changes are associated with tolerance to high S. A better understanding of the rumen microbial response to high S will lead to development of treatments for affected animals.

Title: Rumen Microbial Changes Associated With High Sulfur – A Basis for Developing Treatments for Ruminant Livestock in High Sulfur Water Regions

Statement of Critical Regional or State Water Problem: *Need for Project.* Ruminant livestock consuming water high is sulfur (S) and S-compounds (e.g., sulfate) are prone to poor performance and health. High S can also cause polioencephalamalcia (PEM), a disease state in that can cause 25% morbidity and 25-50% mortality in affected population. Ruminants are especially susceptible to S toxicity because of S metabolism in the rumen by sulfate-reducing bacteria (SRB). High S triggers metabolism by SRB to sulfide, which ultimately increases hydrogen sulfide (H_2S) production in the rumen. It is this increase in H_2S production that is thought to be causal to the poor performance and health (including PEM) of ruminant animals.

Unfortunately, many livestock water sources, especially throughout the semi-arid rangelands of the U.S. and Wyoming, are high in S and S-compounds because of underlying soil conditions or man-made contaminants (e.g., conventional gas and oil water), and are exacerbated by evaporation concentrating S during persistent drought conditions. Unfortunately, producers are typically limited in available water resources, and there are no practical means of treating high S water, especially in range conditions, nor animals suffering the effects of high S water.

The literature is replete with studies aimed at identifying treatments for animals affected by high S. Why, then, have no effective, consistent treatments been discovered yet? Most studies have identified potential treatments *in vitro*, r in laboratory studies using rumen bacterial cultures. However, once these treatments were tested *in vivo*, or in the live animal, limited effects on animal health or performance were typically observed. It is apparent from these studies that *in vivo* and *in vitro* conditions respond differently to high S, indicating the need for a whole-animal approach. A better understanding of how rumen microbial populations (e.g., bacteria) *in vivo* change in response to high S is a critical first step to whole animal studies aimed at targeted treatment development.

Who Would Benefit and Why. Many water sources high in S are still used for livestock production due to lack of alternative available sources, especially in range production settings. Additionally, in many of these areas it is neither feasible nor practical to haul in water low in S. Therefore, identification of an effective treatment for either 1) high S water sources or 2) animals suffering from high S would benefit livestock producers by 1) preventing the health and performance problems associated with livestock consuming high S water, and 2) allowing them to use available water resources despite high S concentrations.

Statement of Results or Benefits: *Information to be Gained and How Information will be Used.* Past studies of changes in rumen microbial population in response to high S have utilized technologies either limited to determining the presence/absence of microbial species, or have utilized *in vitro* culture methods capable of altering bacterial metabolism so that *in vivo* conditions are not truly reflected. We will use DNA sequencing techniques to better identify and quantify changes in rumen microbial populations in response to high S water. We hypothesize that this information is critical for future development of treatments to counteract high S. It has also been well documented in the literature that animals vary in response to high S, with some individuals being highly tolerant, and others lowly tolerant. Through this project we will not only determine general changes to rumen microbial populations in response to high S, but also if the magnitude of those changes differs between animals more tolerant and less tolerant to high S. This information could not only be used for treatment development, but also for management strategies.

If animals could be identified as more tolerant or less tolerant to high S, producers in high S water regions could manage those animals differently.

The results of this research will provide valuable insights into the response by rumen microbes, a necessary next-step in the development of effective treatments for animals affected by high S water. In the short-term, we will also work with the office of the Wyoming State Veterinarian to determine ways to provide information to our targeted audience: livestock producers. *In the long-term, we expect the results of this research to direct future efforts aimed at treatment development to enable livestock producers to better utilize available water resources high in S.*

Nature, Scope, and Objective of the Project: The basic nature of the proposed research is to determine changes in rumen microbial populations in response to high S water. Our objective is to use DNA sequencing to quantify and characterize rumen microbial populations in sheep (our model ruminant) consuming high S water; this approach will allow us to more accurately determine important rumen microbial changes in response to high S. We hypothesize that differences in rumen microbial populations, which are responsible for the breakdown of S and S-compounds, are associated with the variation in animal response to high S. Therefore, in this study our objectives are to 1) determine how rumen microbial populations change in response to high S water, and 2) determine if the extent of those changes are associated with tolerance to high S.

Timeline of Research Activities: ***Year 1*** – Completed animal trial, serum mineral analyses, production data analyses, and DNA extractions and preparations. ***Year 2*** – DNA sequencing (conducted at the DNA Core Laboratory in Columbia, Missouri) completed. Bioinformatic analyses were conducted to identify specific rumen microbial species that change (in abundance) in response to high S water, and importantly identify if such changes infer a “tolerance” to high S. Analysis of ruminal volatile fatty acids (VFAs) was also completed to determine shifts in rumen function. M.S. student Cara Clarkson completed her M.S. thesis in the summer of 2014.

Methods, Procedures, and Facilities: This study used Hampshire wether lambs (n = 40; 6 months of age) maintained at the UW Stock Farm. Lambs were administered a high S water treatment (~3,000 mg/L) over a 28 d trial period; they were individually penned to enable collection of individual feed and water intake. A 28 d trial period was chosen as signs of S toxicity would be more easily observed with the collection of individual feed and water intake; a common sign of S toxicity is decreased feed and water intake. Individual water and feed intake were estimated, along with average daily gain and feed efficiency measures. Blood and rumen fluid samples were collected on d 0 (baseline), d 7, and d 28.

Blood samples were analyzed for S, Cu, and Mo content, and no differences between individual animals were detected. Lambs were selected as highly tolerant (n = 4) and lowly tolerant (n = 4) to high dietary S based on individual water and feed intake, average daily gain and feed efficiency measures, and daily behavioral responses (recorded on a scale of 1 to 5). Rumen fluid samples collected on d 0, d 7, and d 28 (n = 24 samples in total were used for both VFA and DNA analyses. The VFA analysis indicated that intolerant lambs had greater concentrations of isobutyrate and isovalerate, but a lower concentration of valerate. The response in valerate has been observed in other high-S studies, and may indicate a potential adaptation by the rumen microbial population in response to high S. Also, initial concentrations of propionate were greater in tolerant lambs. Propionate is an end-product of starch and sugar fermentation, and considered a more efficient energy source for fermentation. The greater initial concentrations of propionate in tolerant animals may have given rise to greater ability to metabolize high levels of S.

The DNA analysis was used to generate rumen microbial profiles associated with response to high S water. In total, 145 microbial taxa (assumed to be single microbial species) were identified in the rumen fluid, with 29 affected by the tolerance class (tolerant or intolerant) by sampling day interaction; 39 affected by tolerance classification; and 26 affected by sampling day. Species in the *Prevotella* genus were highly detected as would be expected, but there were also numerous specie differences that may be potential indicators of tolerance to high S water. Also, some species responded initially to the high-S water challenge, but then returned to more 'normal' abundances, indicating that certain microbial species are capable of, and important for, adapting to a high S water challenge.

Related Research: *High S Water.* The current NRC recommendation for dietary sulfur is < 0.3% dry matter (DM), with the maximum tolerable concentration estimated at 0.4% DM. Sulfur content in water, however, is typically reported in parts per million (ppm), and the most common form of S in water is SO_4^2. Polioencephalmalacia is associated with water SO_4^{2-} concentrations of ≥ 2,000 mg/L, which when combined with a typical 0.2% DM S feedstuff results in 0.53% DM total dietary S. Therefore, when S or SO_4^{2-} content of water is included in the estimation of dietary S, the total dietary S is often much higher than anticipated.

Survey and field data have consistently shown surface and subsurface water can be high in SO_4^{2-}, particularly throughout the western regions of the U.S. The Water Quality for Wyoming Livestock & Wildlife review reported that of > 450 forage and water collection sites located throughout the U.S., 11.5% exceeded the dietary S concentrations considered safe for livestock. Of those sites, 37% were located in the western U.S., including Wyoming. Drought further exacerbates the high SO_4^{2-} problem, as SO_4^{2-} is concentrated in the water due to greater evaporation and reduced moisture recharge. Finally, conventional oil and gas production can also increase S content within the water source.

Effects on Livestock: Several experimental and field studies have reported reductions in performance of animals exposed to high S drinking water sources. Declines in average daily gain in cattle consuming high SO_4^{2-}water have been reported in both grazing and confined environments. In addition, decreases in feed consumption and overall body weight gain are consistently reported. Polioencephalomalacia (PEM), a prevalent central nervous system disease in cattle and sheep, can also be caused by high S. Clinical signs of PEM include head pressing, blindness, incoordination, and recumbency accompanied by seizures, with young ruminants more commonly affected.

Biological Mechanisms: In ruminants, production of toxic metabolites from S occurs in the rumen. Two classes of bacteria, assimilatory and dissimilatory, are present in the rumen capable of reducing SO_4^{2-}. Sulfide is produced by assimilatory S-reducing bacteria (SRB) and is used immediately for incorporation into metabolic processes. The assimilatory SRB also reduce SO_4^{2-} to create amino acids. Dissimilatory SRB use SO_4^{2-} in respiration pathways and for energy to fuel growth and metabolism. However, in the respiratory pathways excess S^{2-} and H_2S are produced. It is the dissimilatory class of SRB that cause the overproduction of toxic S products leading to cell damage, secondary infections, and the development of sPEM. These bacteria can also produce high amounts of S^{2-}, causing H_2S levels to increase rapidly.

Summary of Progress. To-date, all planned experiments and analyses have been completed (final DNA sequence analysis completed this spring). Additionally, the M.S. student for this project, Cara Clarkson, successfully completed her program. This work has thus far generated one M.S. thesis, two abstracts, and two meeting proceedings. We are currently preparing a manuscript for a peer-reviewed journal (*Journal of Animal Science*); targeted submission is summer of 2015. We have requested a one-year extension for project continuation. We have determined rumen microbial changes in response to high-S water in terms of species abundance. We have proposed to follow this up with determining the functional changes that coincide with these abundance changes. A better understanding of the functional basis for changes in the rumen microbiome is needed to identify potential treatment and(or) prevention strategies for ruminants provided high-S drinking water. RNA sequencing will be used for functional analysis via changes in the rumen microbial transcriptome (i.e. gene expression).

Training. Graduate student training is a priority in the Department of Animal Science. Research endeavors are overseen by faculty and staff, but carried out by graduate and undergraduate students. This project was the thesis project of a M.S. student (advised by PI Cammack) in Animal Science, Cara Clarkson. The student was trained in the areas of animal production, toxicity, genomics, data analysis, and water quality. Ms. Clarkson was responsible for carrying out all aspects of this research project, including both the animal and laboratory components. Together with the PIs, she also helped prepare a manuscript for submission to a peer-review journal. Ms. Clarkson is currently employed in management in the animal industry (Assistant Ranch Manager; Cheley Colorado Camps; Estes Park), and is planning on seeking a Ph.D. program in the near future.

This research also provided a training opportunity for undergraduates employed by PI Cammack. In particular, one undergraduate student served as an intern for this project; she presented her internship experience and research results at the University of Wyoming Undergraduate Research Day. Finally, the continuation of this project has allowed for additional student training through the recruitment of a second M.S. student. Amy Abrams is currently working on DNA and RNA analyses for the project continuation plan. Finally, one Ph.D. student has also been trained in DNA analysis through this project; she is also currently helping train Ms. Abrams in DNA analysis procedures. As such, this project has evolved to being a major part of several graduate students' training.

Publications. M.S. student Cara Clarkson has had one thesis, two abstracts and two proceedings papers stem from this project. She gave an oral presentation on this project at the American Society for Animal Science Western Section in the summer of 2014. She also attended other meetings and had the opportunity to discuss her project and her methods with other experts in the genetics field. Ms. Clarkson, along with Ms. Abrams, also prepared an abstract and proceedings for this year's Western Section meeting. Ms. Abrams will prepare a poster presentation for that meeting.

Information Transfer Program Introduction

Information dissemination efforts included reports and presentations by the Director to State and Federal entities and the private sector. The Director reports annually to the Wyoming Water Development Commission and to the Select Water Committee (of the Wyoming Legislature). Presentations were given throughout the state concerning the research program and project results. The Director serves as the University of Wyoming Advisor to the Wyoming Water Development Commission and attends their monthly meetings. The Director also serves as an advisor to the Wyoming Water Association (www.wyomingwater.org) and regularly attends meetings of the Wyoming State Water Forum.

Publications and other information dissemination efforts were reported by the PIs of the projects funded under this program. The project PIs report to the Institute Advisory Committee on an annual basis. Presentations discussing final results are made by PIs of projects which were completed during the year at the July advisory committee meeting. Presentations discussing interim results are made by PIs of continuing projects at the fall/winter advisory committee meeting. PIs are encouraged to publish in peer reviewed journals as well as participate in state-wide water related meetings and conferences. Publications are listed in the individual research reports.

FY14 OWP Director Information dissemination activities and those reported by research project PIs are listed, by project, in the following paragraphs.

DIRECTOR SERVICE AND PRESENTATIONS: Wyoming Water Forum, Presentation on Water Research Program update. Cheyenne, WY., March 4, 2014, (1) Wyoming Legislative Select Water Committee, Final project funding approval. State Capital, Cheyenne, WY., March 6, 2014, (2) Wyoming Water Development Commission workshop and project approval meetings. Cheyenne, WY., March 6-7, 2014, (3) Wyoming Water Forum, Presentation on Water Research Program update. Cheyenne, WY., April 8, 2014, (4) North American Weather Modification Council, Wyoming Weather Modification pilot program project updates. Reno, NV., April 22, 2014, (5) Weather Modification Association -- Annual Conference, Wyoming Pilot Program presentations. Reno, NV., April 22-24, 2014, (6) UW Water Research Program. WRP Advisory Committee meeting to develop FY2015 RFP topics and research priorities. Cheyenne, WY., April 28, 2014, (7) Wyoming Water Forum, Presentation on Water Research Program update. Cheyenne, WY., May 6, 2014, (8) Wyoming Water Development Commission, presentation of WRP Research Areas from State Agencies, and water project consultant selection approval. Cheyenne, WY., May 9, 2014, (9) UW Water Research Program. WRP Advisory Committee meeting to develop FY2015 RFP. Cheyenne, WY., May 19, 2014, (10) Wyoming Water Development Commission/Select Water Committee joint workshop. Presentation on the UW Office of Water Programs and Water Research Program. Cheyenne, WY., June 4-5, 2014, (11) Wyoming Water Association Board meeting, (Advisor), Cody, WY., June 18, 2014, (12) Wyoming Water Association Summer Water Tour, (Advisor), Evanston, WY., June 19, 2014, (13) WY Weather Modification Technical Advisory Team - Summer 2014 Meeting, Pinedale, WY., July 24, 2014, (14) UW Water Research Program. WRP Priority and Selection Committee meeting to select research priorities and review final project reports. Cheyenne, WY., July 31, 2014, (15) Wyoming Water Development Commission/Select Water Committee joint meeting/summer tour. Sheridan, WY., August 20-22, 2014, (16) Wyoming Water Forum, Presentation on Water Research Program final project reports. Cheyenne, WY., September 9, 2014, (17) Co-Sponsor – Wyoming Big Horn Adjudication Conference. Wind River Indian Reservation, WY., September 10-12, 2014, (18) North American Weather Modification Council annual meeting and tour (Central Arizona Project). Scottsdale, AZ., October 7-10, 2014, (19) Wyoming Water Forum, Presentation on Water Research Program update. Cheyenne, WY., October 14, 2014, (20) Wyoming Water Association Board meeting (Advisor), Casper, WY., October 28, 2014, (21) Co-Sponsor Wyoming Water Association Annual Meeting & Educational Seminar, University of Wyoming Water Research Initiatives. Casper, WY., October 29-30, 2014, (22) Wyoming Water Development Commission/Select Water Committee joint workshop. Presentation on the

UW Office of Water Programs and Water Research Program-preliminary funding recommendation. Casper, WY., November 5-7, 2014, (23) Wyoming Water Research Program Meeting. WRP Advisory Committee review and ranking of water research projects. Cheyenne, WY., November 17, 2014, (24) Wyoming Water Forum, Presentation on Water Research Program Update. Cheyenne, WY., December 2, 2014, (25) Wyoming Water Development Commission/Select Water Committee joint workshop. Presentation of Water Research Program-project selection for FY2015 research funding recommendation. Cheyenne, WY., December 10-11, 2014, (26) Wyoming Water Development Select Water Committee meeting. Presentation on the UW Office of Water Programs and Water Research Program-preliminary funding recommendation for Legislative session. Cheyenne, WY., December 12, 2014, (27) AGU Fall Meeting, Poster Presentation "Relating Snowpack and Snowmelt in Weather Modified Watersheds". San Francisco, CA., December 15-19, 2014, (28) Wyoming State Legislature – Senate Agriculture Committee. Wyoming Water Development Commission (Advisor), Omnibus Water Plan. State Capital Bld., Cheyenne, WY., January 20, 2015, (29) Wyoming Weather Modification pilot program Technical Advisory Team meeting (Super Computer Center). Cheyenne, WY., January 29, 2015, (30) Wyoming Water Forum, Presentation on Water Research Program update. Cheyenne, WY., February 3, 2015, (31) The National Institutes for Water Resources (NIWR) annual meetings. Washington, DC., February 9-11, 2015, (32) Wyoming State Legislature – House Agriculture Committee. Wyoming Water Development Commission (Advisor), Omnibus Water Plan. State Capital Bld., Cheyenne, WY., February 19, 2015.

Project 2012WY81B, MULTI-FREQUENCY RADAR AND PRECIPITATION PROBE ANALYSIS OF THE IMPACT OF GLACIOGENIC CLOUD SEEDING ON SNOW, information transfer activities: (1) Bart Geerts presented an ASCII overview oral paper at the 46th Annual Meeting of the Weather Modification Association, in Reno NV, 23-25 April 2014, (2) Binod Pokharel presented a paper, the impact of ground-based glaciogenic seeding on orographic clouds and precipitation: a multi-sensor case study, at the 46th Annual Meeting of the Weather Modification Association, in Reno NV, 23-25 April 2014, (3) Binod Pokharel presented a second paper, the impact of glaciogenic seeding on snowfall from shallow orographic clouds over the Medicine Bow Mountains in Wyoming, at the 46th Annual Meeting of the Weather Modification Association, in Reno NV, 23-25 April 2014, (4) Xia Chu presented a poster, radar observations and WRF LES simulations of the impact of ground-based glaciogenic seeding effect on orographic clouds and precipitation: Part I: Observations and model validations, at the 46th Annual Meeting of the Weather Modification Association, in Reno NV, 23-25 April 2014, (5) Bart Geerts presented ASCII research update at the bi-annual Wyoming Weather Modification Pilot ProjectTechnical Advisory Team meetings, (6) Bart Geerts presented at the November "ground schools" for the Wyoming Weather Modification Pilot Project, (7) Bart Geerts gave the invited seminar, enhanced water recovery from clouds: is it possible?, at the University of Wyoming Spring 2014 Faculty Senate Award, in Laramie April 16, 2014 and in Casper April 22, 2014, (8) Bart Geerts gave the invited seminar, ASCII overview, results, and lessons learned, at the Denver office of the Bureau of Reclamation, November 25, 2014, and (9) the Associated Press had an article on 5/1/2014, and several news outlets carried the article, upon which Geerts was interviewed regarding this research by ClimateWire in Washington, D.C.

Project 2012WY82B, DECADAL SCALE ESTIMATES OF FOREST WATER YIELD AFTER BARK BEETLE EPIDEMICS IN SOUTHERN WYOMING, information transfer activity: (1) Frank, JM, Massman WJ, Williams DG, Ewers BE, Kipnis E. Does sublimation decline after a spruce beetle outbreak? Agriculture and Forest Meterology Meetings, Portand OR, May, 2014.

Project 2013WY84B, MAPPING ANNUAL SURFACE AREA CHANGES SINCE 1984 OF LAKES AND RESERVOIRS IN WYOMING THAT ARE NOT GAUGED USING MULTI-TEMPORAL LANDSAT DATA, information transfer activities: Tuthill, Z, Sivanpillai, R. 2014. Mapping water bodies with Landsat imagery contaminated with thin layer-clouds. 2014 Wyoming Undergraduate Research Day, Laramie, WY. April 26, (2) McCollum, K, Thoman, MJ. 2013. Transferability of Landsat-derived NDWI Values across space and time. Geospatial Conference of the West 2013, Laramie, WY. Sept 16-19, and (3) Terry, B. 2013.

Characterizing analyst bias in unsupervised classification of Landsat images. Geospatial Conference of the West 2013, Laramie, WY. Sept 16-19 (Note: The last two were not reported in the FY13 annual report).

Project 2013WY87B, RUMEN MICROBIAL CHANGES ASSOCIATED WITH HIGH SULFUR – A BASIS FOR DEVELOPING TREATMENTS FOR RUMINANT LIVESTOCK IN HIGH SULFUR WATER REGIONS, information transfer activity: (1) Clarkson, C.J., H.C. Cunningham, L.E. Speiser, M.J. Ellison, K.J. Austin, and K.M. Cammack, 2014. Effect of high sulfur water on behavior, performance, and volatile fatty acid production in lambs. Presentation, Western Section – American Society of Animal Science.

USGS Summer Intern Program

None.

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	11	0	0	0	11
Masters	8	0	0	0	8
Ph.D.	5	0	0	0	5
Post-Doc.	1	0	0	0	1
Total	25	0	0	0	25

Notable Awards and Achievements

2012WY81B Multi-frequency radar and precipitation probe analysis of the impact of glaciogenic cloud seeding on snow, Graduate student Xia Chu received an NCAR Advanced Studies Program (ASP) doctoral fellowship (host: Lulin Xue), partially funded by the UW Office of Water Programs. She is spending the full year 2015 in Boulder CO.

2012WY81B Multi-frequency radar and precipitation probe analysis of the impact of glaciogenic cloud seeding on snow, Bart Geerts received the Spring 2014 UW Faculty Senate Award. He gave presentations on weather modification at the UW campuses in Laramie and Casper WY.

2013WY86B, Use of Fe(VI) for Removal of Total Organic Carbons (TOC) and Heavy metals from Coproduced Water in Wyoming, Provisional Patents, Fan, M., Argyle, M., Sharrad, M. O. M., Simultaneous Removal of Metals from Fly Ash, U.S. Provisional Patent, 61/518,853 and Fan, M., Tcheunou, P., A Novel Method for Synthesis of Multifunctional Fe^{6+}-Fe^{3+} Agent, U.S. Provisional Patent, 61/505,686.

Publications from Prior Years

1. 2010WY57B ("Development of a Contaminant Leaching Model for Aquifer Storage and Recovery Technology") - Articles in Refereed Scientific Journals - Tuwati, A., Fan, M., and Bentley, M., 2011. Reaction Kinetic Model for a Recent Co-produced Water Treatment Technology, Journal of Environmental Science, Vol. 23, No. 3, PP. 360-365.
2. 2010WY57B ("Development of a Contaminant Leaching Model for Aquifer Storage and Recovery Technology") - Articles in Refereed Scientific Journals - Liu, H., Yang, Y., Kang, J., Fan, M., Qu, J., 2012. Removal of tetracycline from water by Fe-Mn binary oxide, Journal of Environmental Sciences, Vol. 24, No. 2, PP. 242-247.